

R U B B E R

PHILIP SCHIDROWITZ

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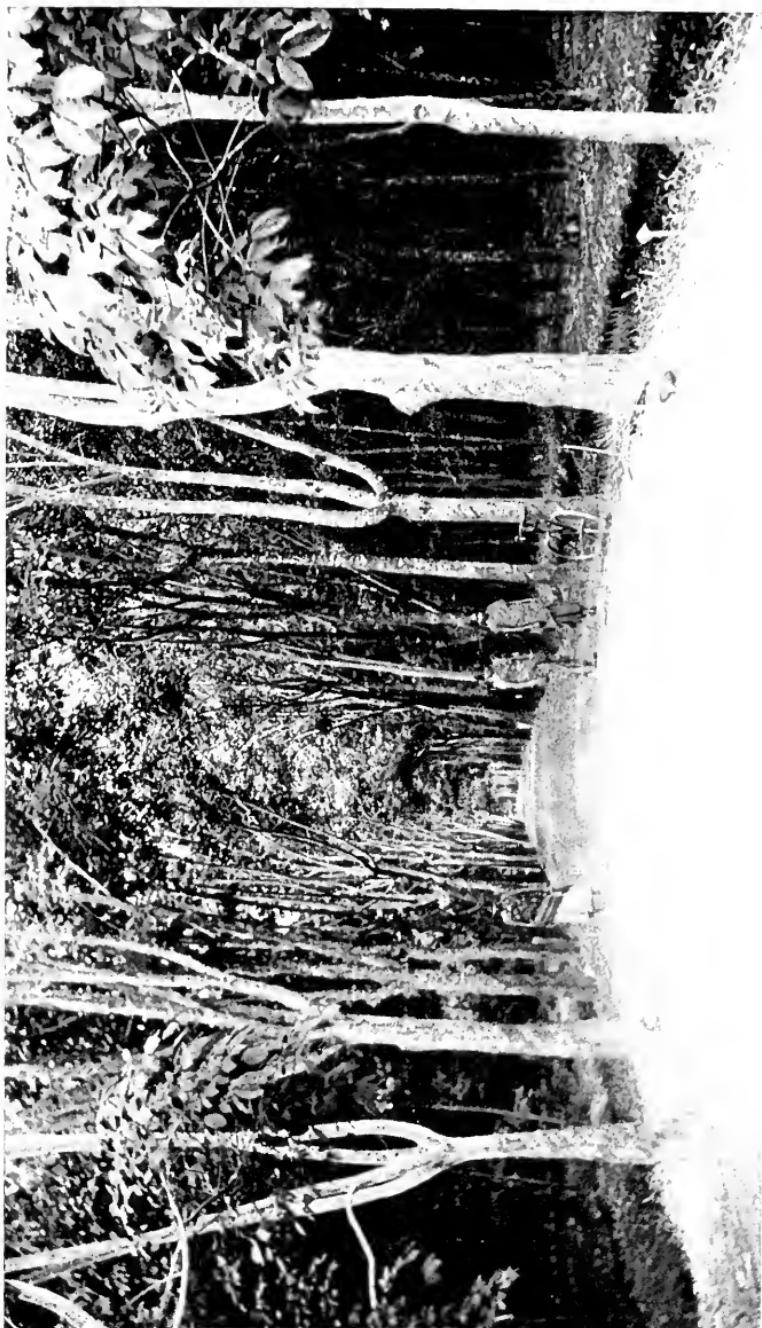
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AVENUE OF 5-YEAR OLD HEVEA TREES (CALEDONIA ESTATE, PROVINCE WELLESLEY)

# R U B B E R

BY

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WITH EIGHTY THREE ILLUSTRATIONS AND DIAGRAMS

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## AUTHOR'S PREFACE

**I**N the autumn of 1910 I delivered, at the Finsbury Technical College, a series of six lectures on Rubber, and, although this book is in no sense a reprint of these lectures, its guiding principle has been the same, namely, to present in a practical, critical, and, I hope, interesting manner, the most important features of the various branches of the rubber industry and of rubber science to the layman as well as to the technologist and student of technical science. While it has not been my aim to treat the subject in encyclopædic fashion, I have, with very few exceptions, dealt only with matters of which I have some practical or first-hand knowledge, and such matters, wherever it appeared to me to be necessary or desirable, I have attempted, to the best of my ability, to handle in a critical spirit.

It may be considered that I have devoted too much space to some, and too little to other sections of the book; that I have, for instance, dealt rather fully with crude rubber, and somewhat curtly with the manufacturing industry; or, again, that I have discussed chemical analysis in outline only, and the mechanical properties of rubber at some length. In

anticipation of such views, I may say that my object has been—while not overlooking general principles—to avoid restating at length that which has been well and fully said in other modern works, and to give ample space—provided the matter appeared to me to be of sufficient general interest—to subjects involving some comparatively recent development or novel principle. I have throughout given ample references to works dealing with special branches of rubber industry or science, which may be consulted with profit by those desirous of obtaining further information on points of detail.

With the exception of a few short extracts from papers that have appeared in the *India-Rubber Journal* and in the *Journal of the Society of Chemical Industry*, the whole of the matter in this volume is newly written. I have to thank my friend Mr. Herbert Wright for kindly reading the proof sheets of the chapter on "The Plantation Industry," and for valuable suggestions.

P. S.

LONDON, June 1911.

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## THE ILLUSTRATIONS

THE illustrations depicting views of and work on Eastern Plantations, etc., are from photographs taken during a tour in Malaya and Sarawak (Borneo) in the summer of 1910. I take this opportunity of expressing my cordial thanks to the Companies which were kind enough, through their representatives, to accord to me the permission to take these photographs, particularly to the Bukit Rajah, Caledonia, Federated Selangor, Tebrau and Vallambrosa Companies in Malaya, and to the United Malaysian Co. in Sarawak. For the African pictures, I am glad to be able to express my indebtedness to the Mabira Forest Co., of Uganda. The Amazon illustrations are reproduced by the kind permission of the proprietors of the *Gummi-Zeitung*. I have to thank my chief assistant, Mr. H. A. Goldsborough, A.I.C., F.C.S., for the plotting and drawing of the viscosity and "tensile" curves, and Mr. Leslie Radclyffe, A.M.I.C.E., for sketches.

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## ABBREVIATIONS

The following abbreviations are employed in this volume :—

- B.* . . . . = *Berichte der deutschen chemischen Gesellschaft.*  
*G.Z.* . . . . = *Gummi-Zeitung* (Berlin).  
*I.R.J.* . . . . = *India-Rubber Journal* (London).  
*I.R.W.* . . . . = *India-Rubber World* (New York).  
*J.S.C.I.* . . . . = *Journal of the Society of Chemical Industry.*  
*Lectures* . . = *Lectures on India-Rubber* (Official account of the  
Conferences held in connexion with the Rubber  
Exhibition, London, 1908. Edited by D. Spence).  
*Z.K.* . . . . = *Zeitschrift für Chemie u. Industrie der Kolloide*  
(Dresden).  
*Loc. cit., p.* . . indicates a reference on a specified page in *this* book.  
*Op. cit., p.* . . refers to a specified page in some other, previously  
cited work.

All temperatures mentioned are *centigrade*, unless otherwise specified.



# RUBBER

## CHAPTER I

### HISTORICAL

**I**T has been generally stated in works on this subject that the first reference to rubber in European writings occurs in a work by a Spanish writer published in Madrid in 1536, but M. L. Tillier<sup>1</sup> in a recent brochure points out that P. Martyr d'Anghiera, in 1525, published a description of some rubber playing balls seen by him in Mexico. M. Tillier also mentions that another Spanish writer, Salahan, in a work with the title *A General History of the Productions of New Spain*, published in 1529, also refers to similar articles, described by him as being made "from a black resin, obtained from a tree called by the natives 'Ulaguhuil.'" To this day, it may here be stated, the *castilloa elastica* is known by the natives of parts of Mexico and Central America as the *Ule* tree. Whether the date 1525, for which we are indebted to M. Tillier, can be improved upon, remains to be seen, but there can be no doubt that the first records concerning the recognition of the remarkable substance known to us as rubber<sup>2</sup> were made by the

<sup>1</sup> *I.R.J.*, 1910, vol. xl. p. 612.

<sup>2</sup> I shall throughout this work employ the term *rubber*, instead of *india-rubber*, and that for two simple reasons. Firstly, because the material, in ordinary speech, is nowadays almost invariably referred to by the shorter term; and secondly, because the prefix has long been misleading, if not entirely meaningless. Rubber does not appear to have come to Europe from the East before the very end of the eighteenth century, yet about 1770 Priestley—the discoverer of oxygen—recommended it for the purpose of erasing pencil marks

Spanish and Portuguese pioneers in the course of their travels in South America and the West Indies. Most of the early observations on record have to do with the use of rubber for the purpose of the ball game already mentioned. The name given by the South American Indians to this game was *batey*, and the ball was termed *batos*. Morris<sup>1</sup> calls attention to the interesting fact that similar balls are made nowadays by the natives in regions as far apart as the Amazon, Central Africa, and Guiana.

I have already (cf. footnote, p. 1) referred to the derivation of the term "india-rubber," but the French synonym *caoutchouc* is also worthy of an explanation. According to W. H. Johnson,<sup>2</sup> *caoutchouc* is derived from *caucho* (a word used in Brazil at the present day to describe a certain commercial variety), and *caucho* in its turn comes from *caa*, wood, and *o-chu*, to run or weep, and so obviously refers to a tree showing some abnormal form of exudation.

The French appear to have been the pioneers in regard to obtaining exact and scientific information concerning rubber-bearing species and the material yielded by them.

The Paris Academy of Sciences in 1731 sent an expedition to South America for the purpose of making certain geographical measurements.<sup>3</sup> This expedition was under La Condamine and Bouguer, and these scientists sent home several reports dealing with rubber in Peru and Brazil. In 1736 La Condamine sent home specimens of rubber, and referred to the fact that in the Province of the Esmeraldas there occurred a tree called *hevea* by the natives, and that they obtained from it a milk-white liquor, which gradually hardened and blackened in the air. He also mentioned that in the Province of Quito the natives coated linen with this

(hence the term "rubber"). It is fairly obvious, therefore, that the prefix "india—" referred to the West Indies and not to India. Nowadays, I may add, comparatively little rubber comes either from the East or West Indies.

<sup>1</sup> Cf. Torrilhon, Seeligmann and Falconnet, *India-Rubber and Gutta-Percha* (transl. from French) (London : Scott, Greenwood), p. 5.

<sup>2</sup> W. H. Johnson, *Para Rubber* (Crosby, Lockwood, 2nd ed. p. 1).

<sup>3</sup> Cf. Torrilhon, Seeligmann and Falconnet, *loc. cit.*

material; that the same tree grew on the banks of the Amazon, and that the natives made boots with it which were water-tight, and which, after having been blackened by means of smoke, had the appearance of real leather. We also gather from him that the natives made by means of moulds rubber vessels for containing fluids. His writings explain how the name *seringueiro* (which obtains to the present day) came to be applied to the rubber collectors. One of the articles made by the latter was a rude syringe, obtained by moulding a rough bottle out of rubber and attaching to its neck a piece of fluted or pierced wood.

#### TECHNICAL DEVELOPMENT

For many centuries, articles such as pouches, boots, and other waterproofed garments have been made by the natives of rubber-bearing districts, and it is on record that the Spanish invaders of South America waterproofed their cloaks with rubber latex. In this connexion a description by H. C. Pearson<sup>1</sup> of articles made by natives in the Amazon districts at the present day is of peculiar interest. Their art appears to have made considerable progress, for in some districts they now mix sulphur with the latex prior to spreading it on the article to be proofed. It is said that articles so produced will keep twice as long as those made by the ordinary vulcanization process, and there is considerable historical justification, therefore, for the process of sulphurizing latex suggested by Mr. M. Kelway Bamber.<sup>2</sup> In 1791 Samuel Peal of London patented a process for waterproofing cloth by spreading it with hot rubber. This appears to have been attended by considerable difficulties, and not to have made much progress. About 1825, however, Macintosh of Manchester produced waterproofed garments by a practicable process, and this method may be regarded as the starting-point of the modern rubber industry, although

<sup>1</sup> *I.R.W.*, September 1910.

<sup>2</sup> Cf. p. 194.

it was not until after the process of vulcanization was discovered by Goodyear in 1839, and independently by Hancock about 1844, that it showed signs of becoming of first-rate technical importance. Among the earlier inventions may be mentioned that of a masticating machine and process by Thomas Hancock of London, who thus introduced the manufacture of rubber sheet, and much improved the method of making "solution," the manufacture of rubber shoes for the first time in Europe in 1825-6, and the attempt in 1832 by the Roxbury India-Rubber Co. (U.S.A.) to make imitation patent leather by means of rubber. The latter was a commercial failure, but it has been stated that the difficulties arising in connexion with this venture formed the impetus which led Goodyear to make his classical researches which finally resulted, as stated, in the discovery of the process of vulcanization.

### *The Proofing Industry*

I have already referred to the early attempts made by natives of rubber-bearing districts to prepare rough water-proof garments, also to the efforts of Samuel Peal in this direction, and I have mentioned the fact that Macintosh of Manchester was the first to produce rubber proofed garments of a practical nature. It was in 1823 that he took out his first patent for proofing textiles. Essentially this process consisted in dissolving thin sheets of rubber in naphtha, spreading the solution so obtained on a marble slab, allowing the solvent to evaporate, and then placing the thin sheet of rubber so obtained on the textile material, to which it was fastened by means of needle and thread. The proofed side of the garment was, however, decidedly sticky, and Macintosh overcame this difficulty by covering the proofed side also with a layer of fabric. In this way so-called "double texture" garments originated. The next development consisted in spreading a masticated dough of rubber upon the fabrics to be proofed by hand, and afterwards passing the

article through heated rollers with a view to obtaining an even surface. This process was cumbersome, and in 1837 Hancock took out a patent for the first spreading machine. All the articles so obtained, however, suffered from the defects inherent in crude rubber, and it was not until after the process of vulcanization was discovered that really satisfactory waterproof garments could be manufactured. The vulcanization of proofed garments was first effected by a hot cure, which consisted in subjecting a fabric coated with a mixture of rubber and sulphur to heat, but this soon gave way, after the discovery of the method of "cold curing" by Parkes in 1846, to the process which consists in subjecting thin rubber layers to the action of chloride of sulphur dissolved in bisulphide of carbon. Subsequently a vapour process, which consists in subjecting the proofed garments to the vapours of bisulphide of carbon instead of to a solution of this substance, and which was much improved by Abbott in 1878, was introduced. Still later (1888) a new form of dry heat process was introduced by Waddington, which consists in passing the cloth spread with rubber dough over a series of rollers in a closed and heated chamber, the time of the passing of the material being so regulated as to effect a cure. This process is still largely used for the manufacture of garments and materials which are not affected by heat. The first successful attempt to make "fancy" garments was that of Charles Moseley, who in 1883 took out a patent for printing on a rubber surface previously treated with starch. Subsequently this process was developed by the use of metallic pigments which give to the material the well-known silk or shot effects.

#### *Rubber Hose*

It was again Charles Macintosh of Manchester and Thomas Hancock of London who were the pioneers in this branch of manufacture. The original hose consisted of an inner coat of solid rubber covered with folds of proofed canvas.

Subsequent developments have resulted in the production of high pressure, vacuum, and other varieties of hose.

### *Rubber Belting*

Prior to the introduction of rubber, machinery belts were made generally from leather, and, as is well known, this material is still very largely used. The first attempt to employ rubber appears to have been made by Allsopp and Forster. It seems to have consisted in employing twisted rubber thread as one of the belting materials. In 1858 Parmelee introduced a process which consisted in coating several layers of textile materials with india-rubber or gutta-percha by means of a spreader, subsequently pressing together the different plies, and then vulcanizing by means of heat and pressure. Later developments have taken the form of impregnating the fibres of the textile materials as such with gutta-percha, balata, or rubber.

### *Rubber Tyres*

The first mention of rubber tyres in general literature is contained in a book by Thomas Hancock published in 1856, in which he suggests the use of rubber tyres for the purpose of avoiding vibration. Prior to this, however, a patent had been taken out for an elastic tyre by Robert William Thompson in 1845, and it has been frequently suggested that this patent anticipated the pneumatic Dunlop tyre. As a matter of fact, it appears to have been satisfactorily proved that Dunlop's invention was developed quite independently of any knowledge of Thompson's work. Thompson's tyre consisted of an elastic belt made of a number of folds of canvas saturated and covered on both sides with india-rubber or gutta-percha in a state of solution. The inner tube so obtained was to be protected by a cover built up round the tyre, made by riveting together circular segments of leather and bolting these to the tyre. There was also provision by means of a pipe passing "through the

tyre" for inflating with air. As far as can be ascertained, very little practical use was made of Thompson's invention. In 1856 a solid tyre composed of cloth, or other fibrous material, and rubber sheet in alternate layers was made by W. Coles Fuller. This tyre was made up on a cylinder fastened to the wheels by means of flanges. The introduction of the bicycle about 1869 gave the necessary impetus for the further development of the solid, and subsequently of the pneumatic, tyre, but the history of this development has been so frequently recorded, and is so readily accessible elsewhere, that I do not propose to deal with it further here.

### *Elastic Thread*

In 1830 Thomas Hancock obtained a patent for cutting rubber into thin strips for making elastic springs for gloves, braces, and similar articles. In 1832 Dumeste applied for a patent for a machine for making elastic thread of different sizes. In 1836 Westhead invented an improved method of cutting rubber by means of a revolving cutter working in a spiral or helical direction towards the centre of a block of rubber wound round on to a cylinder. In the same year Hertley took out a patent for making cut sheet. It was not until after the process of vulcanization was discovered, however, that elastic thread of a really serviceable nature was made. Messrs. Archibald Turner of Leicester, who established a factory in that town in 1844, appear to have been the pioneers in the manufacture and employment of vulcanized thread, and they seem to have been the first to appreciate the fact that vulcanized thread is so elastic that it can be woven with cotton or other material into a web. At one time elastic thread was very largely used for making "springside" boots, but these have almost entirely gone out of fashion. This material is, however, very largely employed for other purposes nowadays, for instance for surgical bandages, belts, braces, and so on.<sup>1</sup>

<sup>1</sup> For a number of the facts in the above technical review I am indebted to a series of articles in the Quart. Cent. Number of the *I.R.J.*

*Vulcanization*

From the above brief sketch of the technical development of the manufacturing branch of the rubber industry it will have been gathered that it would have been permanently confined to moderate proportions, but for the discovery of the process of vulcanization. The theory and practice of vulcanization will be discussed in some detail in Chapters XI. and XII., but in order that the development of the india-rubber industry since its discovery may be fully appreciated I think it advisable to say a few words in this connexion here. I have already referred to the fact that we owe the discovery of vulcanization to the independent researches of Goodyear of Newhaven, U.S.A., and to those of Thomas Hancock of London, respectively. They found that by subjecting crude india-rubber to the combined action of sulphur and heat, that it not only gained greatly in strength and elasticity, but that it also became remarkably insensitive to changes of temperature. I may here say that crude rubber, when subjected to a degree of cold not exceeding that of an ordinary winter temperature becomes quite stiff and inelastic, and conversely becomes sticky and loses its elasticity when subjected to a moderate heat. It is, moreover, adhesive at ordinary temperatures. Goodyear's process consisted in mixing the masticated crude rubber with finely divided sulphur and subsequently heating the dough so obtained. Hancock, on the other hand, found that the desired change of physical properties of crude rubber could be obtained by dipping this material into a bath of molten sulphur. The process of cold vulcanization discovered by Parkes, as stated, in 1846, consists in subjecting crude rubber to the action of a solution of sulphur chloride in carbon bisulphide. This process, however, is only suitable for goods of a very moderate thickness.

## SCIENTIFIC DEVELOPMENT

The first experimental work of a scientific nature on rubber appears to have been that of Herissant and Macquer,<sup>1</sup> who in 1763 published a paper on the roots of some rubber species of Cayenne. In 1763 they sent a memoir to the Paris Academy of Sciences dealing mainly with the behaviour of rubber towards various solvent media. Among other chemists and technologists who occupied themselves with rubber problems during the period 1769 to 1820 were Fourcroy, Berthollet, Priestley, Grossart, and Charles. As early as 1832 Lüdersdorf observed that if sulphur was added to a solution of crude rubber in turpentine the solution was rendered non-adhesive, and later he based on this a claim to the discovery of the process of vulcanization.

During the years 1826-1854 Hancock carried out experiments on the degree of permeability of rubber to water, and in 1866 Graham published a paper on the rate of diffusion of various gases through rubber membranes. Early work on the dry distillation of rubber was carried out by Himly and Bouchardat. Subsequently Greville Williams, Tilden, Weber, and others occupied themselves with work in this direction, and the data gathered by these investigators formed the groundwork on which the greater part of the researches of Ipatiew, Tilden, Harries, etc., connected with the constitution and synthesis of the rubber hydro-carbon, were based.

The elementary composition of rubber was first studied by Faraday, Ure, Williams, Berzelius and Adriani, and later by Gladstone and Hibbert<sup>2</sup> and Weber.<sup>3</sup> The latter came to the conclusion that the presence of a small proportion of oxygen in crude rubber, which was ascribed by Gladstone and Hibbert to "heating," was due to the presence of a specific substance, corresponding closely to the formula  $C_{30}H_{68}O_{10}$ , and that this was identical with the "insoluble

<sup>1</sup> Torrilhon, &c., *loc. cit.* p. 2.      <sup>2</sup> *J. Ch. Soc.*, 1888, vol. lxviii. p. 680.

<sup>3</sup> *The Chemistry of India-rubber* (London : C. Griffin, 1902).

substance" always present to some extent (3 to 6 per cent.) in Para Rubber. It had, prior to this, been widely held that this "insoluble substance" was one of the two modifications in which rubber was supposed to exist, these "modifications" or "isomers" being regarded respectively as the cause, on the one hand, of the adhesive properties, and, on the other hand, of the "nervous" or tensile attributes of the material. Weber regarded this theory as being entirely disproved by his work, and although Spence,<sup>1</sup> in recent times, has shown that Weber was probably wrong in regard to the composition of the "insoluble substance" which, as a matter of fact, contains a high proportion of nitrogen, there can now be no doubt that his (Weber's) views on the main question, *i.e.* as to the non-existence of "adhesive" or "nervous" modifications, were entirely correct. The general result of the researches on the composition of the rubber molecule has been to establish as a practical certainty the fact that it possesses the formula  $(C_{10}H_{16})_n$ .

The *constitution* of the rubber molecule and its *synthesis* will be dealt with in another place, but it may here be stated that the modern work on this subject dates from the last decade of the nineteenth century, and consists broadly, on the one hand, of the researches of Tilden, Wallach, Ipatiew, Hittorff, Euler, and others, on the constitution of isoprene, and the relationship of this body to, and its transformation into rubber, and, on the other hand, of the work of Harries and his school on the fission products obtainable from rubber and its derivatives. The products obtainable by the action of the halogens and of nitrous and nitric acids on rubber have been studied in modern times chiefly by Gladstone and Hibbert, Weber, Harries and Paul Alexander, and will be referred to later.

The discovery of the process of vulcanization naturally led to much scientific discussion as to its nature, but although theories were abundant, the experimental data on record prior to Weber's entry into this domain were exceedingly

<sup>1</sup> *Journ. Inst. Comm. Research in Tropics.* Reprint No. 13.

meagre. In the course of the nineties Weber contributed a series of brilliant experimental researches on this subject, which led him, later, to propound his *Outlines of a Theory of Vulcanization*.<sup>1</sup> Weber came to the conclusion that both hot vulcanization and cold curing represent purely chemical-addition-processes, and until quite recently his views have been regarded as substantially correct. Taking as a basis certain admitted facts and recent work on vulcanization by E. Stern, Hinrichsen, Bysow and Hübener,<sup>2</sup> Wolfgang Ostwald<sup>2</sup> has recently (1910) published a series of papers in which he advances the view that all the known phenomena characteristic of vulcanization are explainable by the assumption that it represents a process of colloidal adsorption.

Some of the earlier researches on the physical properties of rubber have already been referred to. The first systematic examination of its remarkable "tensile" properties, however, appears to have been carried out by Stévert<sup>3</sup> in 1868. It is curious that this research, which is a model investigation of its kind, has been comparatively neglected in the literature on the subject. Stévert from his experimental data was able to deduce certain fundamental laws, which still form the basis of many of the mechanical tests to which rubber articles are submitted. Among the later workers in this field, Shedd and Ingersoll, Bouasse, Schwartz, Memmler and Schobb, Dalen and Schopper may be mentioned.<sup>3</sup> The development of analytical science as applied to rubber work is chiefly due to R. Henriques, who in 1892 to 1894 published a series of brilliant papers on this subject.

<sup>1</sup> *Loc. cit.* p. 82.

<sup>2</sup> For literature references, see Chapter XI.

<sup>3</sup> For literature references, see Chapter XI.

## CHAPTER II

### PRODUCTION AND CONSUMPTION OF RUBBER

FROM the preceding chapter it will have been gathered that the india-rubber industry proper is of comparatively modern origin. The point is amply confirmed by the statistics bearing on the question, and may be illustrated by way of the following figures relating to imports of crude rubber into the United Kingdom :—

#### IMPORTS OF RUBBER INTO THE UNITED KINGDOM

1830—23 tons.	1850—381 tons.	1870—7656 tons.	1890—13,200 tons.
Average : 1907—8—29,889 tons.	1909—35,000 tons.	1910—43,848 tons.	

#### PRODUCTION

It is a little difficult to arrive at exact figures regarding the world's production of crude rubber, particularly in view of the rapidly increasing supplies from certain quarters ; but there is very little doubt in my mind that the figures most frequently quoted in this connexion—varying from 70,000 to 75,000 tons—are too low. During the year ending 30th June 1910, the United States alone imported over 45,000 tons (exclusive of gutta, balata, Jelutong, etc., but inclusive of Guayule), and during the year 1910 the United Kingdom took some 43,000 tons.

This gives us a total of 88,000 tons, of which perhaps 7000 tons (re-exports) overlap, leaving say 81,000 tons. We may safely assume that only a very small proportion of the

United Kingdom re-exports went to Havre, Antwerp,<sup>1</sup> or Bordeaux, yet these ports alone received in 1909 some 12,000 tons between them. We are forced to the conclusion, therefore, that the United States and the chief ports of Europe are between them receiving something like 85,000 to 90,000 tons. Obviously this is being "produced," and only a small proportion can be accounted for by withdrawals from stocks. There is, further, no great risk in assuming that the figures for production and consumption correspond pretty closely, and a consideration of the figures for consumption lead us to much the same result as do those mentioned above.

In 1909-10 the United States *retained for consumption* over 42,000 tons, the United Kingdom in 1910 over 20,000 tons, Germany some 14,000 tons, France 4600<sup>2</sup> tons—a total of well over 80,000 tons. The statistics for the remaining European countries are not readily available, but it is well known that Canada, Austria-Hungary, Belgium, Italy, and Russia, etc., all use large quantities of rubber, certainly, I should say, not less than 5000 to 8000 tons between them. This again gives a total of 85,000 to 88,000 tons for 1910. In making these calculations I have not taken into account any drawing on reserve stocks, but these, in any case, could not to any material extent affect the figures. A consideration of the known sources of production leads me to believe that the present (1911) production is at the rate of 86,000 to 93,000 tons (exclusive of certain low grade gums). I estimate that this is produced as follows:—

1 and 2. Brazil, Peru, and Bolivia . . . . .	40,000 to 41,000 tons.
3. Other South American countries, Mexico, and Central America . . . . .	15,000 to 17,000 ,,
4. Africa . . . . .	15,000 to 17,000 ,,
5. Ceylon, Malaya, Java, Sumatra, and Borneo . . . . .	14,000 to 15,000 ,,
6. Miscellaneous . . . . .	2,000 to 3,000 ,,

<sup>1</sup> Of the 4686 tons imported by Antwerp, 3492 tons were from the Belgian Congo.

<sup>2</sup> See pp. 16-19.

In connexion with this estimate I may point out that:—

1. The receipts at and shipments from Para, of Para and Peruvian sorts, for the past three years have been as follows:<sup>1</sup>—

Year.	Receipts at Para.	Shipments from Para.
1908 . . .	38,200 tons.	38,066 tons.
1909 . . .	39,050    "	39,280    "
1910 . . .	38,160    "	37,990    "

2. Considerable quantities of high grade rubbers are exported from Peru and Bolivia direct (Caucho, Mollendo, Peruvian Para, etc.). The figures obtainable appear to indicate that these exports amount to about 2000–3000 tons.

3. The United States, in the period already referred to, imported over 10,000 tons of rubber from Mexico. The production of Mexican Guayule at present appears to be about 12,000 to 14,000 tons.<sup>2</sup> Considerable quantities of rubber are exported from various Central and South American States (Ecuador, Columbia, Guiana, etc.).

4. While there has been some falling off of "Africans" during the past few years, the conditions of production are, owing to improved organization, rapidly improving over considerable forest areas. A number of African plantations are already in bearing, and many others are approaching the producing stage. I do not think, therefore, that any further material decrease is likely to occur for the present. The exports of West African sorts in 1910<sup>3</sup> is computed to have been 14,800 tons. The estimate I have made of 15,000 to 17,000 tons for the *whole* of Africa for 1911 is therefore, I think, not unreasonable.

5. It is generally agreed that the production of the Eastern plantations during 1911 will not be far short of 15,000 tons.

The figures given above do not include inferior (very

<sup>1</sup> *I.R.J.*, 1911, vol. xli. p. 162.

<sup>2</sup> Cf. pp. 107 *et seq.*

<sup>3</sup> *I.R.J.*, *loc. cit.*

resinous) raw materials such as "Jelutong" or "Pontianac." The production of these is very large, and seeing that the United States alone, for the year ending 30th June 1910, imported over 23,000 tons of this class of material, and that very considerable quantities are used in Europe, the total output at present is probably not far short of 40,000 tons, corresponding roughly to 4000 tons of rubber.

What the future production of rubber may be is largely a matter of speculation, but increases may be looked for in the following directions:—

1. *From the Plantations.*—In the absence of any wholesale calamity, there should be produced<sup>1</sup> from the Eastern plantations in 1915–16 at least 70,000 to 80,000 tons. The plantations in other parts of the world (Africa, Mexico, Brazil, West Indies, etc.) may yield another 10,000 tons.

2. *Industrial Rubbers.*<sup>2</sup>—An increase of, certainly, 5000 to 10,000 tons (from Jelutong, Guayule, and vines) should take place.

3. *Selected Forest Areas worked on Plantation Lines.*—A probable increase of 1000 to 2000 tons is to be expected.

On the other hand, we may expect that perhaps 10,000 tons of low grade or improperly prepared rubbers from Africa, Asia, and South America will disappear. On balance, therefore, and assuming that the Brazilian supplies and Guayule do not fall off materially, there will, in 1915–16, be an increase of production over 1911 of, roughly, 60,000 to 70,000 tons, that is to say, a total production of 145,000 to 160,000 tons.

## CONSUMPTION

The most important rubber-consuming countries are the United States, the United Kingdom, Germany, and France. As a rough approximation it may be stated that the United States consume three-sixths of the world's rubber, the United Kingdom and Germany each one-sixth, and the other countries the remaining sixth. I have based this rough

<sup>1</sup> For details, see Chap. V.

<sup>2</sup> See Chap. VII.

calculation on the fact that the latest available figures indicate a consumption for the United States of, roughly, 42,000 tons; for the United Kingdom 15,000 tons; for Germany a similar amount.

*Extent of the Industry in the Leading Countries.*

The following figures will give a general idea of the importance of the rubber industry in the United States, the United Kingdom, Germany, and France respectively:—

I.—THE UNITED STATES

IMPORTS OF CRUDE RUBBER

(Official Statement for the Fiscal Years ending 30th June.<sup>1</sup>)

From	1907-08.	1908-09.	1909-10.
	lb.	lb.	lb.
United Kingdom . . .	6,809,622	12,825,192	15,556,981
Germany . . .	2,821,194	4,503,286	6,528,147
Other Europe . . .	6,883,473	7,598,809	9,598,411
Central America . . .	992,198	861,636	1,424,449
Mexico . . . .	9,269,443	15,460,365	23,486,384
Brazil . . . .	32,645,173	43,993,670	39,510,920
Other South America . .	1,537,887	1,964,114	2,503,683
East Indies . . .	1,237,487	1,127,686	2,419,956
Other Countries . . .	36,683	25,137	15,750
Total <sup>2</sup> . . .	62,233,160	88,359,895	101,044,681
Import value . . .	\$36,613,185	\$61,709,723	\$101,078,825
Average per pound . .	58.8 cents.	69.8 cents.	\$1.00
NET IMPORTS (RETAINED FOR CONSUMPTION)			
Imports . . . .	lb.	lb.	lb.
Imports . . . .	62,233,160	88,359,895	101,044,681
Exports . . . .	4,110,667	3,791,961	6,492,947
Net imports . . .	58,122,493	84,567,934	94,551,734
OTHER UNITED STATES IMPORTS			
Balata . . . .	584,552	1,157,018	399,003
Gutta-percha . . . .	188,610	255,559	784,501
Waste Rubber . . . .	16,331,033	20,497,695	37,364,671
Gutta-jelutong . . . .	22,803,303	24,826,296	52,392,444 <sup>3</sup>

<sup>1</sup> Cf. *I.R.W.*, 1st September 1910.

<sup>2</sup> The total for 1906-7 was 76,963,838 lb.; for 1905-6, 57,844,345 lb.

<sup>3</sup> Value \$2,419,223. Of the total quantity, 51,828,083 lb. were imported from the Straits Settlements (*i.e.* transhipped from Singapore), 539,721 lb. from the United Kingdom, and 24,640 lb. from the Dutch East Indies direct.

## EXPORTS AND IMPORTS OF MANUFACTURED GOODS

*Exports*

Articles.	Value.
Belting, packing, and hose . . . . .	\$1,960,825
Boots and shoes . . . . .	1,984,739
Other goods . . . . .	5,115,331
Total . . . . .	<b>\$9,060,895</b>

<i>Imports</i>
Value . . . . .

Value . . . . .      \$1,154,347

## II.—THE UNITED KINGDOM

## CRUDE RUBBER

Year.	Imports.		Re-Exports.		Retained for Consumption.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
1910	cwt. 876,968	£ 26,096,988	cwt. 467,872	£ 14,853,063	cwt. 409,096	£ 11,243,925
1909	700,062	£ 14,138,204	397,924	£ 9,118,084	302,238	£ 5,020,120
1904-8 (average)	587,781	£ 9,302,990	334,129	£ 5,858,488	253,652	£ 3,444,502
1907	667,294	£ 10,934,759	...	...	...	...

## RUBBER

II.—THE UNITED KINGDOM—*continued*DETAILS OF IMPORTS FOR 1909<sup>1</sup>

From	Quantity.	Value.
	cwt.	
Brazil . . . . .	308,742	£8,626,639
Peru . . . . .	20,518	731,408
French colonies . . . . .	69,601	757,246
Other foreign countries . . . . .	174,152	1,398,348
Total foreign . . . . .	582,013	11,513,641
British possessions . . . . .	118,049	2,624,563
Total . . . . .	700,062	£14,138,204

EXPORTS AND IMPORTS OF MANUFACTURED GOODS,  
1909 AND 1910

Articles.	Exports Value.		Imports Value.	Re-Exports Value.
	1909.	1910.	1910.	1910.
Boots and shoes . . .	£205,668	£191,688	£194,109	£15,076
Waterproofed garments.	295,184	498,775	7,377	1,076
Miscellaneous goods . .	1,576,000	1,816,930	not stated.	not stated.
Cables (other than telegraph and telephone).	289,342	442,537	169,199	12,484
Telegraph and telephone cables . . . .	744,140	2,280,910	269,268	16,662
Totals . . . .	£3,110,334	£5,240,840	...	...

<sup>1</sup> Details for 1910 not issued at date of writing.

III.—GERMANY<sup>1</sup>

## CRUDE RUBBER

	1909.	1910.
	tons.	tons.
Imports . . . . .	15,500	18,700
Re-exports . . . . .	4,000	4,900
Balance retained . . .	11,500	13,800

## MANUFACTURED GOODS

*Exports, 1910 (chief articles only)*

	Quantity.	Value.
	tons.	£
General soft rubber goods . . . . .	865.3	412,000
Ebonite . . . . .	273.4	87,600
Proofed garments . . . . .	644.7	296,450
Cables (lighting, aerial telegraph, etc.).	2,569	314,750
Submarine, etc. cables . . . . .	32,678	2,369,150

## IV.—FRANCE

## CRUDE RUBBER AND GUTTA

	1909.	1910.
	tons.	tons.
Imports . . . . .	13,184	16,850
Re-exports . . . . .	8,243	12,217
Balance retained . . .	4,941	4,633

<sup>1</sup> *G.Z.*, 1911, vol. xxv. pp. 680 and 804.

## CHAPTER III

### GENERAL NATURE OF THE RUBBER INDUSTRY

THE rubber industry as a whole may be conveniently and naturally subdivided into three sections, namely—(1) The crude rubber industry; (2) the manufacturing industry; (3) the waste rubber industry. Each of these sections will be dealt with in its proper place, but a few general remarks which will serve to give the reader a bird's-eye view of the industry as a whole are, I think, desirable.

#### I. THE CRUDE RUBBER INDUSTRY

A very few years (less than a decade) ago a discussion of the crude rubber industry from a broad standpoint might have been limited to a few brief sentences. Industrially regarded, there was very little either of technical or of scientific interest connected with it. It was necessary for the dealer and manufacturer to have a considerable empirical experience of the numerous brands of rubber on the market, classified as they were, and still largely are, simply according to their geographical origin. Such knowledge is still essential, but whereas there was, for all practical purposes, no attempt at a true classification according to the botanical or chemical nature of the rubber, there is now a slow but sure movement in this direction. In view, however, of the, for the most part, extremely crude and haphazard methods of preparation which formerly prevailed and which are not yet by any means obsolete, a classification such as I have referred to

would have had but little practical value. Large quantities of raw material are still prepared by the old unscientific, uncleanly methods, and for some time to come this will be unavoidable, as will also be, for the time being, the continued geographical or territorial classification of such material, but the rise of the plantation industry has taught dealers and manufacturers that rubber can, and must be, prepared in a cleanly fashion, that the product should be practically pure, and that only one true classification is possible, namely, that based on the botanical nature of the tree, shrub, or creeper. Whether, in its turn, the botanical classification will disappear as increasing knowledge shows us to what extent rubbers of different botanical origin are physically and chemically different, and to what extent improved methods of culture and preparation can minimize these differences, is an open, but interesting, question. As a striking illustration of the rapid developments of the plantation industry, I may instance the fact that in C. O. Weber's classical work on the *Chemistry of India-Rubber* published in 1902, I have been able to find absolutely no reference to it; and as a parallel illustration of the remarkable influence which it has already had on the crude rubber industry generally, I may refer to the fact that not only in scientific journals, but also in popular publications, discussions regarding, or references to, the merits of different species, or of different methods of preparation, are by no means uncommon at the present time.

*Source of Rubber.*—Rubber is generally derived by a process of coagulation from a fluid contained in a special cell system, the so-called laticiferous system of various trees, creepers, and shrubs. It also occurs, but not frequently, in the solid state, as a deposit in the woody fibre of certain species, for instance, in the guayule shrub. The laticiferous system (which is distinct from, and must not be confused with, the cell system bearing the ordinary tree sap) of most rubber-bearing species lies between the outer bark and the cambium. By cutting through the outer bark and into the latex cells in an appropriate manner, the latex may be

obtained in the shape of a white to cream coloured, more or less viscous, fluid. This operation is termed tapping, and will be referred to further in subsequent chapters. After the latex has been obtained the rubber, which is contained in it in the form of a negative emulsion, must be separated from it, and this process, which is termed coagulation, is carried out, according to the species, district, or other conditions, in a variety of ways. Methods of coagulation will be dealt with in their proper place, but I may here say that there is a general tendency towards standardizing or approximating the numerous methods still employed, and that the time is probably not far distant when it will be recognised that there is only one correct system of coagulation for each individual latex. If a popular analogy for the coagulation of the rubber latex is desired, it may be compared to the process which results in the formation of a clot of cheese from milk, or to the preparation of curds and whey. After the rubber clot has been obtained, it is generally purified and dried to a greater or less extent, and is then ready for export. In the case of the well-known Para rubber the processes of coagulation and drying go hand in hand.

## 2. THE MANUFACTURING INDUSTRY

When the crude rubber, obtained roughly in the manner described, reaches the manufacturer, he subjects it, according to its degree of purity and dryness, to further processes of purification and desiccation. After it has gone through these operations it is in the form of a rough crinkled sheet or crepe, which is ready for the next process, namely, that of "mixing." This consists in rendering the rubber plastic by means of heat and mechanical action, and then mixing with it the sulphur necessary for the vulcanizing process and such other ingredients as may be desirable. The mixed dough of rubber, sulphur and other substances is then vulcanized either in a mould, in a press, or in the open, either in live steam, by hot air, or by the combined action of pressure and

heated metal surfaces. This is the general process mostly employed for so-called "mechanical" goods; for other classes of material, different methods, which will be duly described, are applied.

### 3. THE WASTE RUBBER INDUSTRY

The quantity of waste rubber which comes into the market is very large, and this may be utilized in several ways. In the first place, it may be merely cleansed, ground up, and used afresh in (generally) relatively small quantities, in a new mixing. Secondly, the rubber, after it has been thoroughly purified, may be subjected to one of the numerous "reclaiming" processes which have for their object, obtainable by chemical or mechanical means, the removal from the rubber of as much as possible of the sulphur and other foreign ingredients, and so to bring the rubber as nearly as possible to its original crude condition. Thirdly, the waste rubber may, after cleansing, be simply ground up, and then "re-formed" by means of heat and heavy pressure in a mould.

## CHAPTER IV

### WILD RUBBER

#### OCCURRENCE OF RUBBER-BEARING SPECIES

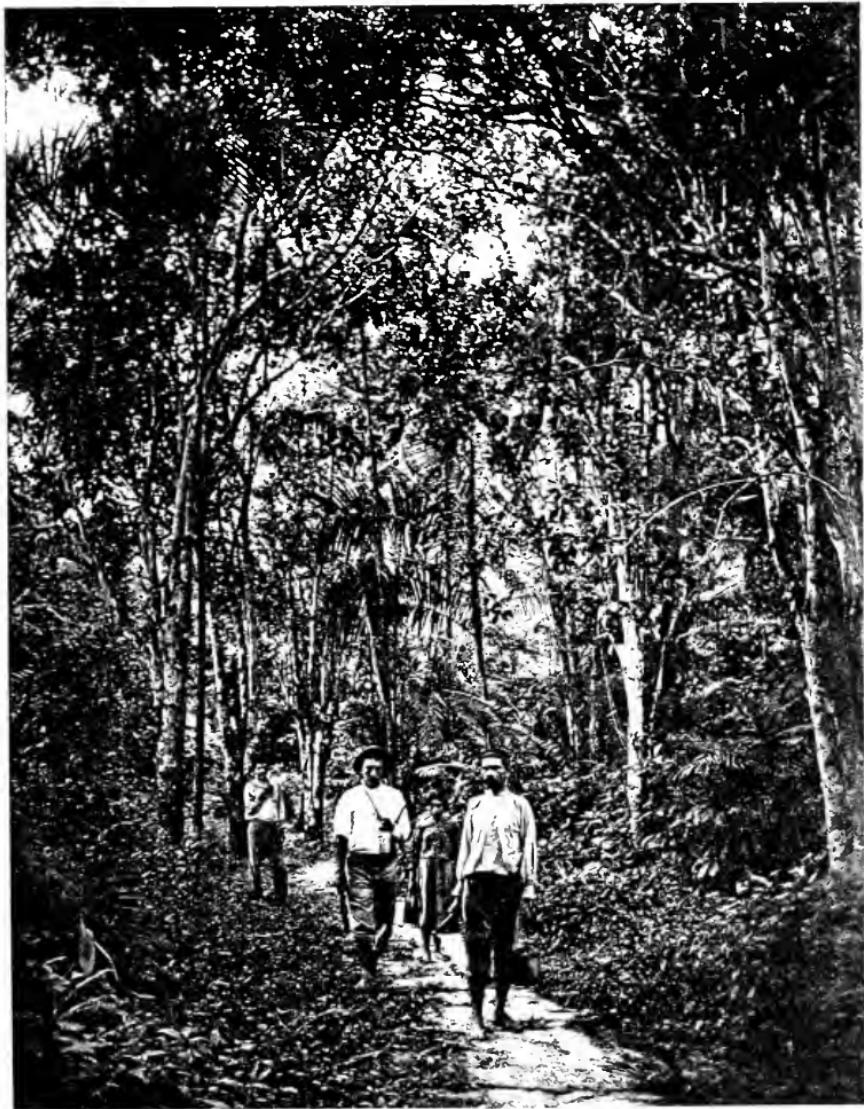
RUBBER-BEARING species are indigenous to considerable tracts of the tropical and sub-tropical zones of South and Central America, Asia, Africa, and Australia. Favourable conditions are a moist climate with high and equable temperatures and a fairly copious rainfall. Although the nature of the soil is of importance, certain species thrive surprisingly well in soils which would be regarded as poor from the point of view of planting many other tropical products.<sup>1</sup> Rubber-bearing species are very numerous, but I propose to refer only to those which have some technical importance.<sup>2</sup> The chief orders are (*a*) The Euphorbiaceæ; (*b*) Apocynaceæ; (*c*) Urticaceæ; (*d*) Compositæ.

#### *a. EUPHORBIACEÆ*

The most important genus of this order is the *Hevea*, and from the species *Hevea brasiliensis*, Muell. Arg., about 60 per cent. of the world's total output of rubber is obtained.

<sup>1</sup> For particulars regarding soils, climate, etc., see Chapter V.

<sup>2</sup> For a full list, see Herbert Wright, *Journal of the Society of Arts*, April 26, 1907, pp. 618 *et seq.*



SIRINGUITIROS BRINGING IN TALEX (AMAZON)



*I. H. Brasiliensis* OR PARA RUBBER

The species is indigenous over large tracts of South America, principally in the areas watered by the Amazon and its tributaries, namely, in the States of Para and Amazonas, Brazil. It is almost unnecessary to add that it has been employed practically to the exclusion of all other species on the Eastern plantations. In its natural state the *H. brasiliensis* is a large tree growing to a height of 100 feet, with a diameter up to 40 inches. It has been frequently stated that so far no more than a small proportion of the trees in the vast forests bordering the Amazon, the Rio Negro, the Rio Madeira, etc., has been exploited, but however that may be, there can be no doubt that the number of trees is very great. To what extent it will be possible to open up and make accessible the great "Hinterlands" of the forests fringing the rivers of Brazil, Peru and Bolivia, is a problem which the future alone can decide, but the construction of the Madeira-Mamoré railway has formed a promising beginning, and is an indication that the difficulties are not altogether insuperable.

## PARA RUBBER

*Economic Conditions*<sup>1</sup>

The bulk of the rubber from the Amazon district is derived from tracts of forest bordering on that river and its tributaries. Concessions to work specified and delimited areas are obtained by individuals or companies on lease from the State, and the working of any area not previously surveyed by the State authorities is illegal. The number of private owners or lessees and sub-lessees is very con-

<sup>1</sup> Cf. Sandmann, *Tropenpflanzen*, 9, 407 *et seq.*, for a detailed and exceedingly interesting account of conditions on the Amazon; also H. C. Pearson, *The Rubber Country of the Amazon* (The India-Rubber World Publishing Co., New York, 1911).

siderable. With regard to corporate undertakings, there were organized during the years 1906-7 alone<sup>1</sup> fifty-two companies with a capital of about 2 millions sterling. The concessions (termed locally *seringals*) vary considerably in size, the usual method of computing this being according to the number of *estradas* running through the estate. The *estradas* are paths of a convenient length, running in zigzag fashion from and to the encampment or factory, so cut as to lead past 100 to 150 trees. The trees may be as far apart as 100 yards, but frequently clumps of two to six trees are found close together. After the *estradas* have been opened up, it is reckoned that one *seringueiro* (rubber worker) can deal with two *estradas*.

The *seringueiros* are mostly recruited from the States of Ceará and Maranhão,<sup>2</sup> and as the wastage due to death, sickness and desertion is very high, it is as a rule necessary to provide for roughly eighty labourers for a *seringal* on which the actual work can be carried out by fifty men. The financing of a *seringal*, owing to the exceedingly high prices of food stuffs, the great distances of many of them from the base of operation, and the advances which have to be made to the *seringueiros* for outfit, etc., is a costly operation. A loan of, roughly, 500 *milreis*<sup>3</sup> is the usual advance made to the *seringueiro*, and the fitting out of an expedition for a *seringal* of 100 *estradas* will therefore cost something like £2500. Transport, the cutting of paths, building of huts and factory and other expenses necessary before the *seringal* is a "going concern," may, according to Sandmann (*loc. cit.*), practically double this sum, that is to say, a capital sum of £5000 is necessary for the *working expenses* of an estate containing say 10,000 to 15,000 trees. The advances made to the *seringueiros* are, of course, repay-

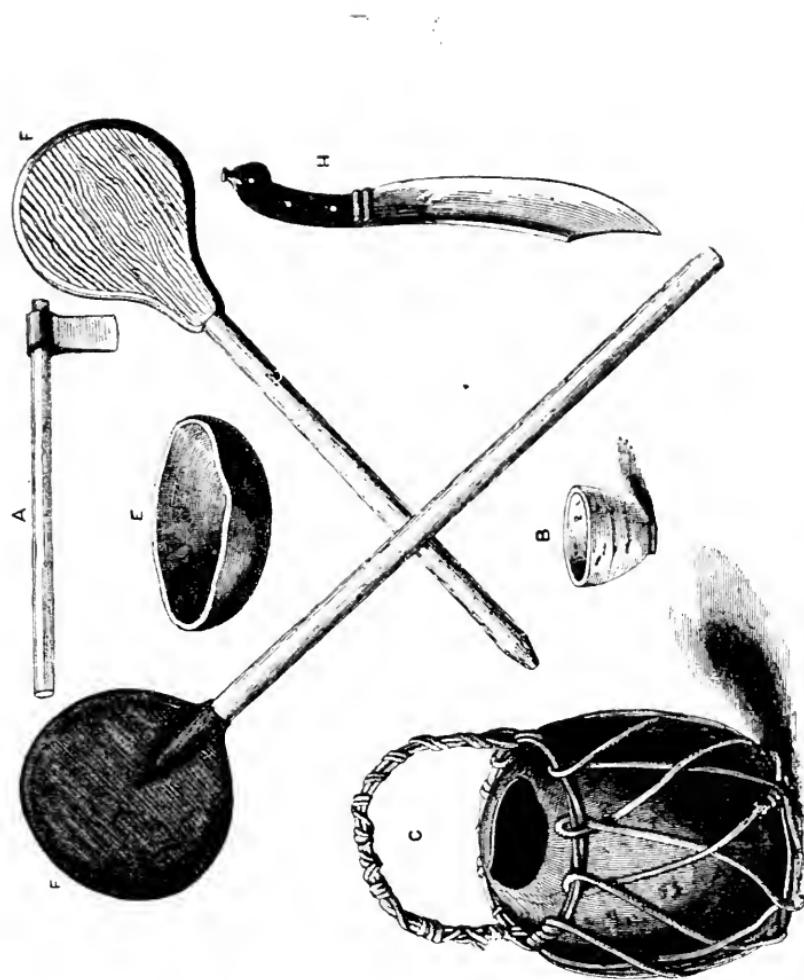
<sup>1</sup> J. C. Oakenfull, *Brazil in 1910*. (Edited by the Commission of Economic Expansion in Brazil.)

<sup>2</sup> This applies mainly to the labour for the upper reaches; in the "Islands" district—at the mouth of the Amazon—a considerable proportion of the labour is local.

<sup>3</sup> The *milreis*=about 1s. 4d.

IMPLEMENTS USED BY BRAZILIAN RUBBER COLLECTORS

A, 'MACHADINHA' (SMALL AXE) FOR TAPPING. B, COLLECTING CUP. C, COLLECTING VESSEL INTO WHICH CONTENTS OF CUPS ARE POURED. E, SAUCER BY MEANS OF WHICH LATEX IS Poured OVER PADDLE F DURING SMOKING PROCESS. THE PADDLE F (TO THE LEFT) IS SHOWN COVERED WITH A LAYER OF RUBBER.





able, and a high rate of interest (10 to 15 per cent.) is charged upon them, but the death or desertion of a *seringueiro* represents a total loss, and as the loan is repaid by off-setting it against the sum receivable by the *seringueiro* on account of the rubber produced by him, sickness is almost as fatal to the repayment of the loan as death. The actual owner or sub-owner (*patrao*) of a *seringal* rarely finances his own property. Advances are generally made to him by the large dealers and export firms (*aviadores*) at Para and Manaos. The method of payment to the *seringueiro* varies in different districts; he may receive say two-thirds of the market value at Manaos or Para, or 80 per cent. to 90 per cent. of the net profit obtained by the sale of the goods by the *patrao*, or the whole of the net profit minus that accruing from a certain weight of rubber (about 75 lb. is a usual figure) for each *estrada*. A good average yield for a six months season<sup>1</sup> is 800 lb., but on favourably situated *seringals* an industrious *seringueiro*, by collecting daily  $1\frac{3}{4}$  to  $2\frac{1}{4}$  gallons of latex from the two *estradas* under his care, can produce daily 9 to 11 lb. of rubber, or 1500 to 1700 lb. in the season. After allowing for repayment of advances to the *patrao*, this will leave him with a profit of perhaps £50 to £60 for the season's work. As a rule, however, the profit he makes is barely sufficient to cover the living expenses of his family during his absence at the seat of operations, and very often the *seringueiro* remains in the debt of the *patrao*. On the whole, his lot is not an enviable one.

According to Sandmann (*loc. cit.*), the main item in the cost of production of Amazon rubber at the present time is the living expense of the *seringueiro*, and this is stated to amount to no less than three milreis per kilo, or nearly 1s. 10d. per lb. of rubber collected. This is chiefly due to the absurdly high price of food stuffs. Sandmann gives

<sup>1</sup>The majority of the *seringals* are situated in low-lying country which is more or less flooded, and therefore unworkable during the rainy season. As a rule it is impossible to work longer than six to eight months in the year.

the following comparative prices of certain staple articles of food :—

	In Rio de Janeiro.	On the Piurinyi (Amazon).
Flour . . .	58 to 85 reis	1000 reis
Sugar . . .	250 to 500 "	1500 "
Rice . . .	200 to 290 "	1500 "
Coffee . . .	32 to 36 "	2000 "
Dried Meat.	600 "	3000 "
Beans . . .	130 to 180 "	1200 "

In former times—before the rubber production of the Amazon attained to anything like its present scale—considerable quantities of rice and other food products were actually exported from the Amazon district, and Sandmann, therefore, believes that by throwing a certain proportion of the available land under cultivation, and by better organization, it would be feasible to reduce the living cost of the *seringueiro* from about 1s. 10d. (as at present) to about 5½d. The mortality and sickness would, according to the same authority, be much reduced, if the food supplied were of a better quality than is at present the case, and if efforts were made to open up the foot-hill districts lying beyond the inundation areas. This, moreover, would permit of work during the whole of the year, and so lead to a more economical and regular general scheme of operations. Sandmann believes that if these conditions were fulfilled, there is no reason why the Amazon should not produce rubber at about 8d. per lb., provided that the present system of taxation were abolished. According to Mr. Oakenfull (*loc. cit.*), the taxes levied at present are as follows: (1) An export tax levied at Para of 15 per cent. to 25 per cent. *ad valorem*, according to quality; (2) local taxes at Manaos<sup>1</sup> amounting to about 28 per cent. of the value when put on board. In addition to the taxes, the river freights from Manaos to Para amount to something like 3½d. per lb.

<sup>1</sup> This, of course, only applies to "up-river" rubber.



CURING PARK RUBBER (AMAZON)

THE MAN TO THE LEFT IS "SMOKING" A LARGE BALL OF "FINE" RUBBER. (SEE PL. 6.)  
THE SECOND SERINGUEIRO IS FREEKARING "NEGO-HEADS." (SEE PL. 5.)



With regard to the perhaps somewhat optimistic views of Sandmann on the *possible* cost of production on the Amazon, it is necessary to point out that, notwithstanding the very high prices prevailing since 1909, the Amazon output has actually declined for the period 1909–11. This would scarcely appear to indicate an improvement in general economic conditions, but rather the reverse.

#### TAPPING AND COLLECTION OF LATEX

The trees are tapped by means of a small iron hatchet (the *machadinha*) having a blade about one inch broad, the incisions taking the form either of V cuts or of oblique lines. Two days prior to the commencement of the tapping operations proper, a cut is made at a height of about 10 feet, the *seringueiros* having discovered that this has the effect of stimulating the flow of latex. In other words, the phenomenon of "wound response" has been known for many years past to the South American tapper. The first tapping proper is made at a height of about 6 to 7 feet, subsequent tappings at intervals of roughly 1½ to 2 inches beneath the first incision, until the base of the tree is reached. About thirty-five consecutive daily tappings are therefore necessary to complete a tapping line (*arracao*). A fresh tapping line is then commenced at a horizontal distance of approximately 2 *palmas* (17 to 18 inches) from the first one. In some cases, however, this procedure is varied, four or five V's or oblique cuts being made daily. The collecting cups (*tigelinas*) are fixed to the tree by means of moist clay, or some similar method. After the *seringueiro* has completed his tapping round of the *estrada*, he goes over the same ground again in order to collect the latex.

According to Sandmann (*loc. cit.*), it is not considered advisable to tap trees less than 9 to 10 inches in diameter.<sup>1</sup>

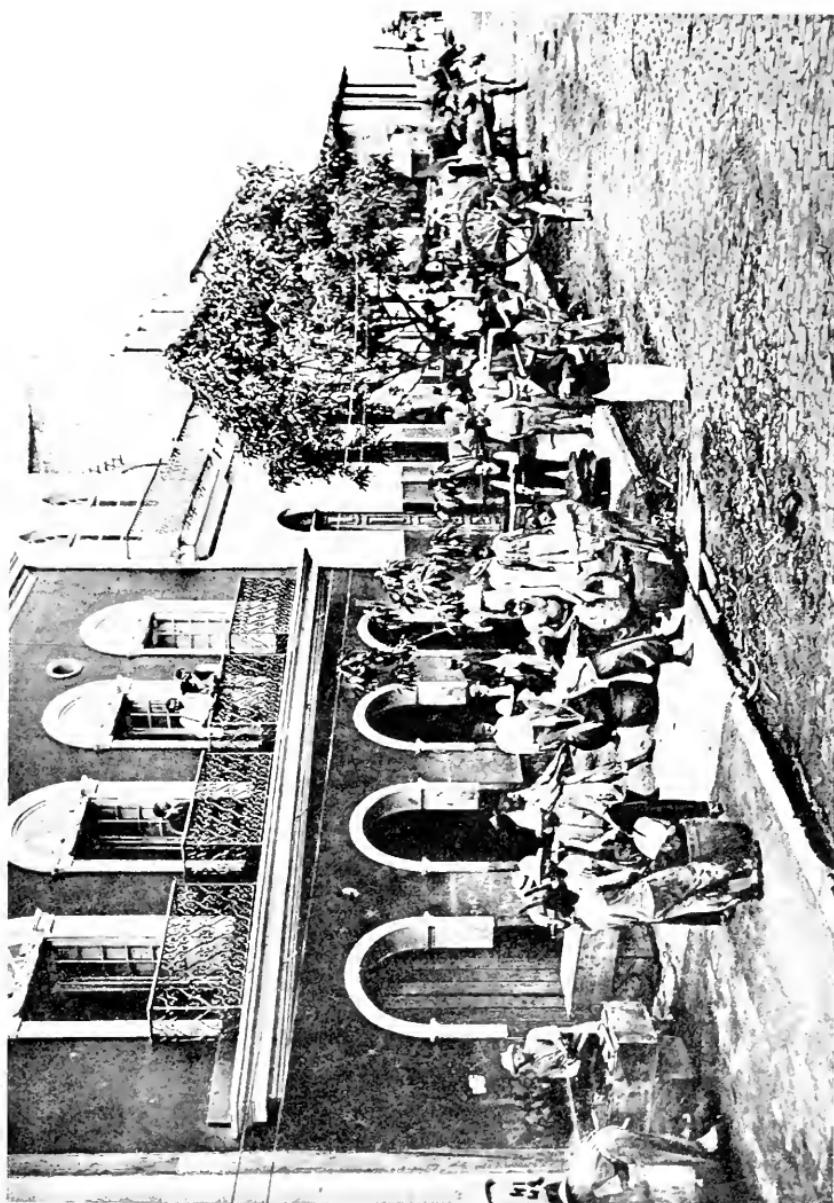
<sup>1</sup> There is no reason why trees of much smaller girth should not be tapped, except that the careless methods of the *seringueiro* would lead to wholesale destruction of the younger, and therefore more delicate plants.

A normal *estrada* will contain say 120 trees of an average diameter of 10 inches, yielding altogether about  $\frac{1}{2}$  to  $1\frac{3}{4}$  gallons of latex daily, the average being a little over one gallon. This corresponds to a daily yield per tree of about  $1\frac{1}{2}$  ounces (42 grms.). In a tapping season of one hundred and forty days an average *estrada* will, therefore, produce roughly 140–160 gallons of latex, corresponding to some 850 lb. of (wet) rubber. It would appear, then, that the Amazon tree will give an annual yield of about 5 lb. dry rubber, but it is at least doubtful—I have not been able to collect any data on this point—whether any large proportion of the trees show as high a yield as this over a succession of years.

After the latex has been transferred from the collecting tins to pails, and from the latter to a flat basin, it is coagulated by means of a smoking process. This is accomplished much as follows:—In a small brazier a fire is made, consisting largely of material giving a dense smoke rich in the products of dry distillation of woody matter (creosote, tarry matter, acetic acid). For this purpose the fruits (nuts) of the *urucuri* palm (*Attalea excelsa*) are considered particularly suitable, and as a rule these are available in large quantities.<sup>1</sup> A mandril, consisting of a long wooden rod or paddle, is so disposed, one end on a cross piece, the other on the operator's knees, that it can be rolled either over the top of the chimney—and so be exposed to the full volume of smoke—or over the latex-containing basin. The operator then pours a small quantity of latex over the wooden paddle or rod,<sup>2</sup> thus forming a thin film of liquid. This is rotated in the smoke until it sets. A fresh quantity of latex is then poured on to the first film, smoke is again applied, and so on, until a biscuit or ball of rubber of the required size (20 to 100 lb. is the general average of weight), consisting of innumerable thin layers

<sup>1</sup> In the lower reaches of the Amazon. Above Manaos the smoking appears to be carried out entirely with hard wood.

<sup>2</sup> Large balls or "biscuits" are made on a circular rod, small balls on the "paddle."



SAMPLING, SORTING AND PACKING RUBBER AT MANAOS (AMAZONAS)



tightly adhering to one another, is formed. The ball is then removed from the mandril and is ready for export, forming the "fine Para" of commerce.

There are two main districts in which fine Para rubber is prepared—(a) The "Islands" at the mouth of the river, (b) the "up-river" regions, near and above Manaos. "Islands" rubber as a rule is of the variety known as *soft-cure*, up-river rubber as *hard-cure*. It is not always easy to state positively whether a given sample is *soft* or *hard* cure. The main difference is that indicated by the names. Imperfectly cured loaves (both "soft" and "hard" cure) go by the name of *entre-fine*.<sup>1</sup>

The scraps of rubber adhering to the bark of the trees, coagulating in the cups, etc., are compressed (unsmoked) into irregular masses and go by the name of "Negroheads." Up-river "negroheads" are generally denominated "scrappy." Island negroheads go by the name of "Sernamby." Then there is a third variety of negrohead, the *Cameta*, coming from the district of that name in South-west Para.

Among the other main commercial varieties of *H. brasiliensis* may be mentioned—

- |  |  |
|--|--|
| (1) Matto-Grosso, fine and entre fine              | } from the Province of Matto-Grosso,<br>Brazil. All unsmoked.  |
| (2) , , , virgin                                   |  |
| (3) , , , negroheads                               |  |
| (4) Mollendo (Bolivian Para).                      |  |
| (5) Peruvian (fine, ball, etc.).                   | <i>Note.</i> —Some "caucho"<br>and "Peruvian ball" consist of <i>Castilloa elastica</i> and <i>C. Ulei</i> . |
| (6) Caucho (partly from Brazil, partly from Peru). |  |

Although the rubbers referred to above consist mainly of *H. brasiliensis*, the latices of other *Hevea* species, such as *spruceana*, *itauba*, *discolor*, *similis*, and *speciosa*, are also

<sup>1</sup> In curing "fine Para" the operator is expected to separate the pieces of "scrap" which form in the latex prior to the commencement of the coagulation process. Careless *seringueiros* frequently do not trouble to do this, and the result is that each piece of scrap in the biscuit may form a centre of infection, besides producing an irregular appearance. This is the cause of the production of the class of Para termed "entre-fine."

employed to some extent in their preparation. Very little definite information in this regard is, however, available.

The "fine hard" brands are of remarkably good quality, and their value still constitutes the standard of price whereby the market price of other rubbers is fixed.<sup>1</sup>

## II. *Manihot*

The most important species of this genus are *M. Glaziovii* and *M. dichotoma* (Jequie manihot). It is characteristic of the *Manihots* that they will thrive in relatively poor, stony soil, and at altitudes at which most other rubber species cease to grow. The most important commercial variety is the so-called Maniçoba or Ceara rubber (Maniçoba, Ceara Scraps) emanating from the Province of Ceara, Brazil. The output of this rubber has increased very rapidly during the past decade, rising from (in round figures) 473 tons in 1901 to 2682 tons in 1905. Since the latter date there has been a gradual falling off. There is some difficulty in collecting the latex, owing to its viscous character and to its property of rapidly coagulating.<sup>1</sup> The natives allow the latex to coagulate naturally as it flows down the tree, and the bulk of the rubber is collected in tears and scraps which are stripped from the bark. A certain amount of latex reaches the ground, and this is collected either in leaves or directly from the soil. The result is that Maniçoba rubber varies a good deal in quality, and mostly contains much extraneous matter, such as bark, sand, and promiscuous dirt. It is, however, a rubber of exceptional strength, and, properly prepared, of very high quality.

## III. *Sapium*

Some species of this genus, e.g. *S. tolimense* (commercial varieties Colombia Virgen, Carthagena Scraps), similarly to

<sup>1</sup> For information regarding *Manihot* as a plantation tree, and the application of plantation methods, see p. 104.

*Manihot*, grow well at considerable altitudes. Properly prepared the rubber is of fair quality.

#### IV. *Micandras*

Principally *M. syphonoides*. Occurs chiefly on the Upper Amazon. The latex is believed to be used to a considerable extent (mixed with *Hevea*) in the preparation of scrappy Negroheads and of other "Para" varieties.

#### b. APOCYNACEÆ

The bulk of the African rubbers belong to this order, and the main genera are *Funtumia*, *Landolphia*, and *Clitandra*.

##### I. *Funtumia*

The only species which can at present be regarded as of commercial importance is *F. elastica*, Stapf. Other species, such as *F. latifolia* and *F. africana*, yield very resinous, low grade latices, which are, however, employed to a considerable extent by the natives for the purpose of adulterating superior gums.

*F. elastica*, also known, on account of the peculiar sheen of the freshly cut surfaces of recently coagulated material, as "Lagos silk rubber," forms a considerable proportion of the brands known in the trade as Gold Coast Lumps, Ivory Coast Lumps, Niger Niggers, Benin Lump, and of some Congo and Cameroon varieties. The tree occurs naturally in considerable numbers on the Gold and Ivory Coasts, in Uganda, and in other parts of tropical Africa.

The average mature forest tree has a circumference of 30 to 40 inches, and rises to a height of 40 to 50 feet. In the Mabira Forest, trees with a circumference of 80 inches and a height of 100 feet are not uncommon. *Funtumia* rubber has lately come into prominence, owing to the fact that the Mabira Forest Co. of Uganda has evolved a system

of preparing it from latex derived from forest trees on plantation lines. As *Funtumia* latex coagulates readily on boiling, it is not surprising that most native methods are based on this fact. A decoction of the leaves of *Bauhinia reticulata* is also employed occasionally, as this facilitates coagulation by heat considerably. *F. elastica* rubber, when properly prepared, is of very high quality, particularly in regard to mechanical strength.

## II. *Landolphia*. Vine Rubbers

The *Landolphias* are creepers or vines, mostly of a considerable size (up to 6 inches in diameter), occurring very profusely on the Congo, in parts of the East and West Coasts, Central Africa, Abyssinia, etc. The most important species are *L. owariensis*, *L. Heudelotii*, *L. Thollonii*, and (principally in Madagascar) *L. sphaerocarpa* and *L. Pierrei*.

Practically all the more important brands of African rubbers which are not derived from *Funtumia* or *Clitandra* species are obtained from *Landolphias*. Among the best commercial brands are the Congo varieties (Red and Black Kassai, Upper Congo balls, Equateur), certain Madagascares (Virgin sheets, Pinky), and Sierra Leone Niggers.

The methods employed by the natives for coagulating vine latices are of the most diverse kind. Thus Red Kassai is stated to be obtained by smearing the latex on the body and allowing the natural heat to evaporate the water. Subsequently the rubber is stripped off. Black Kassai is prepared by a combined boiling and smoking process. Some of the "Ball" rubbers are obtained by applying a coagulant such as salt to the cuts made in the vine, drawing the thread of rubber thus obtainable to form a core, and subsequently winding more and more thread round the core until a ball of the desired size is made, employing a certain

amount of salt at intervals so as to maintain continuous coagulation.

Vines do not readily lend themselves to tapping in the ordinary way. They are generally cut down and bled to death, or the wood is allowed to dry and the rubber subsequently removed by a process of maceration (see "Industrial Rubbers," Chap. VII., p. 114).

### III. *Clitandra*

Another genus of creepers widely distributed in parts of Africa is that of the *Clitandra*. They occur in profusion mainly on the Gold Coast and on the Congo.

### IV. *Hancornia*

In certain Brazilian provinces (principally Bahia and Pernambuco) the *Hancornia speciosa*, which yields the rubber known commercially as *Mangabeira* (also as Bahia, Matto-Grosso sheets, etc.), occurs in considerable quantity. In 1904 over 850 tons of this rubber was exported from Brazil. It is generally coagulated by means of alum, and is of medium quality.

### V. *Dyera*

*Dyera costulata* or Jelutong. See chapter on "Industrial Rubbers."

## C. URTICACEÆ

The most important species of this order occur in tropical Asia, in Mexico, and in South and Central America.

### I. *Ficus*

*Ficus elastica* or "Rambong" rubber is indigenous mainly in Asia (Burmah, Ceylon, Malaya, Java, India, etc.). The principal commercial brands are Assam, Rangoon, Java,

and Penang. *F. elastica* latex has a tendency to coagulate rapidly on the tapping lines, and is generally collected in the form of "tears" or "scraps." It is a hardy tree, and the rubber when properly prepared is of excellent quality, but the yield is poor. It will be referred to further in connexion with the Plantation Industry (p. 102).

## II. *Castilloa*

The *Castilloa* species (principally *Castilloa elastica* and *Castilloa Ulei*) represent the indigenous rubber trees *par excellence* of Mexico and Central America. Most of the Peruvian "Caucho" rubber is derived from *C. Ulei*, whereas Caucho Negro (Ecuador), Mexican Strips and the different "West Indian" or "Centrals" (from Costa Rica, Nicaragua, Honduras, Salvador and Guatemala) are prepared from *C. elastica*. The methods of coagulation vary a good deal, soap and alkaline solutions, salt, the juices of various plants (*e.g.* of the bindweed), all finding application. *Castilloa*, when properly prepared, is a high class rubber (see Chapter VI.).

## d. COMPOSITÆ

*Parthenium argentatum*. Guayule. See chapter on "Industrial Rubbers," p. 107.

### GENERAL CHARACTERISTICS OF WILD RUBBERS

#### *Quality and General Attributes of Different Species*

There are very marked differences in the quality of the various rubbers described above. These differences are attributable partly to the inherent properties of the various latices from which they are derived and partly to the methods of collection and preparation.

Two main factors determine the value of a rubber, namely, its chemical purity and its physical properties. The

chief "chemical" impurities are natural impurities, such as water (moisture), resins, proteid, ash, and matters insoluble in rubber solvents, and adventitious impurities such as mechanically admixed earth, bark, stones, etc. In regard to physical properties the main variations are in regard to strength and vulcanizing capacity.

#### *Differences due to inherent properties of the latex*

If we confine ourselves to the consideration of mature healthy trees or plants, there is in regard to chemical composition, in the narrower sense of the term, no very great difference between the latices derived from the more important species. That is to say, it is possible to prepare from the latex of any of these species a rubber which in regard to caoutchouc content, resin, proteid, and ash, does not differ very materially from that prepared from any of the other latices. Thus from *Hevea*, *Castilloa* and *Manihot* species it is possible to prepare rubbers containing not more than 1.5 to 3 per cent. of resin, from *Ficus* and *Funtumia* and the better *Landolphia* species rubbers containing from 5 to 7 per cent. calculated in each case to dry substance. It is possible to prepare all these rubbers so that they may reach the market in practically a dry condition and containing not more than roughly 3 to 5 per cent. jointly of ash, proteid and other non-rubber and non-resin substances. The physical properties of rubbers prepared from the main species (assuming in each case that they are dry and properly prepared) exhibit wider differences than do the chemical properties, but it is by no means certain that improved methods of preparation will not in the future tend to minimize these differences also. As far as our present knowledge goes with regard to pure and properly prepared rubbers, the best of the *Funtumia* and *Landolphia* and *Manihot* species seem to show the greatest mechanical strength, then follow the *Hevea* and *Ficus*, and then the *Castilloa* and *Sapium* species. The differences in regard

to physical and physico-chemical properties between the various species are of considerable interest, inasmuch as it would appear from the work of Harries and Gottlob that the complex caoutchouc molecule in some of the African varieties (probably *Landolphia* and *Funtumia* species) is not identical as regards complexity and disposition of the simple molecules with the molecule of the *Hevea* species. These, however, are questions which will be considered when I come to deal with the chemistry and physics of rubber as such.<sup>1</sup>

If I have laid considerable stress on the great similarities in some respects of rubbers properly prepared from different species, and differences in other respects, it is because these questions have an important bearing on the remarkable and scientific evolution of the rubber industry in recent times, and because they are, in my opinion, destined to play a still more important rôle in the future. A few years ago it would have appeared rash to state that a pure, commercially satisfactory rubber, differing in commercial value only within relatively narrow limits, could be obtained from practically any of the main species. Anyone inspecting the various "cakes," "balls," "lumps," "niggers," "thimbles," etc., emanating from Africa, or some of the native products from Asia and tropical America, would scarcely believe that most of these are prepared from latices which, if properly handled, would yield rubbers as clean and as pure as, and differing little in commercial value from, fine hard Para on the one hand or the best plantation products on the other. It is mainly due to the work of the chemist, stimulated by the rise of the plantation industry, which in its turn is largely indebted to the efforts of economic botanists and planters, that this change in our views and this important addition to our knowledge has come about. Indeed, speaking of the principal species, one is tempted to think that within a measurable space of time it will be possible to say of rubber, as the Highlander is reputed to have said of whisky, that

<sup>1</sup> See Chap. X.

some is good, and some is not quite so good, but that there is none that is bad.

*Differences due to methods of preparation*

It will be observed from the foregoing paragraph that, at any rate as far as chemical purity is concerned, the differences due to inherent properties of the original latices of the main species are not very great. When we come to methods of preparation, however, the situation is by no means so satisfactory. Much wild rubber is still prepared in a very crude manner, and this is likely to be the case for some time to come. Practically all wild rubbers contain, in addition to a considerable proportion of moisture, a varying quantity of mechanical impurities, such as bark, sand, stones, and dirt. Such rubbers have to be thoroughly cleaned before they can be used in the factory. The process of cleaning consists substantially in passing the rubber, after it has been cut up, through the washing rolls (see p. 75), and thus subjecting it to a combined process of washing and disintegration. Subsequently the rubber is dried. The loss which native or "wild" rubbers show after this process has been completed generally varies from 10 to 50 per cent. or even more. In the case of "Fine Para" sorts, the "washing loss," as it is technically termed, consists mainly of moisture, but the loss of inferior grades is largely accounted for by the presence of bark, sand, stones, and dirt.

The following table is designed to show roughly the loss that may be expected from some of the more important "wild rubbers":<sup>1</sup>—

Name.							Loss on Washing.
Fine Para (hard and soft cure)	.	.	.	.	.	.	12 to 20 per cent.
Negroheads	.	.	.	.	.	.	20 to 40 ,,
Maniçoba	.	.	.	.	.	.	28 to 30 ,,
Matto-Grosso	.	.	.	.	.	.	15 to 30 ,,

<sup>1</sup> For comprehensive washing loss tables, cf. Spence, *Official Account of Proceedings, Rubber Exhibition, London 1908*, pp. 30 *et seq.*; Weber, *The Chemistry of India-Rubber*.

## RUBBER

Name.	Loss on Washing.
Mangabeira . . . . .	30 to 35 per cent.
Upper Congo, Red and Black Kassai, } Equateur (better qualities) }	6 to 12 ,,
African "Niggers" (Soudan, Conakry, } Sierra Leone, Niger, etc.) }	15 to 40 ,,
Madagascar Pinky . . . . .	18 to 20 ,,
Madagascar Niggers . . . . .	40 to 50 ,,
Assam . . . . .	15 to 40 ,,
Borneo . . . . .	25 to 50 ,,

The actual loss in weight connoted by the "washing loss" is not, however, the only commercial disadvantage displayed by improperly prepared wild rubbers. Unsound methods lead to "tackiness" and general deterioration of the rubber as such, and to the presence of more resin and other non-rubber substances (not removable by washing) than is either necessary or desirable.

## CHAPTER V

### THE PLANTATION INDUSTRY

**I**T is perhaps no exaggeration to suggest that the most important occurrence in the rubber industry since the discovery of the process of vulcanization is the foundation and development of the Eastern plantations. In 1875 Wickham was commissioned by the Indian Government to obtain a supply of *H. brasiliensis* seeds in the Amazon valley, and from the seeds secured by him and from small parcels obtained from other sources, substantially the whole of the sixty to a hundred million trees now growing in the East have been raised. In 1876 the first large batch of seeds was planted in Ceylon, but the following twenty years constituted a purely experimental period, and it was not until several years of the present century had passed that planting on a really industrial scale commenced. The evolution of the industry may be gauged by the following figures illustrating the development in Ceylon:—

#### APPROXIMATE ACREAGE UNDER RUBBER IN CEYLON<sup>1</sup>

Year.	Acreage.
1890	300
1895	550
1898	1,250
1904	11,000
1907	150,000
1910 (beginning)	190,000

<sup>1</sup> Wright, *Hevea Brasiliensis*, p. 4.

## RUBBER

The following is an estimate of the total acreage under planted rubber in various parts of the world<sup>1</sup> :—

Country.	Acreage.
Ceylon . . . . .	200,000
Malay Peninsula <sup>2</sup> . . . . .	400,000
Java, Sumatra, and Borneo . . . . .	200,000
S. India and Burmah . . . . .	35,000
German Colonies . . . . .	45,000
Mexico, Brazil, Africa, and W. Indies . . . . .	<u>100,000</u>
Total . . . . .	980,000

According to the Resident-General's report, the number of rubber estates in the Federated Malay States at the end of 1909 was 377, their acreage 500,431, and the planted area 196,953 acres. The increase in production in the Malay Peninsula, which, I may perhaps add, is at the present time far and away the most important plantation district, may be gauged by the following figures, issued by the Director of Agriculture for the Federated Malay States :—

## PRODUCTION IN THE MALAY PENINSULA, 1906-9

	1906.	1907.	1908.	1909.
	lbs.	lbs.	lbs.	lbs.
Selangor . . . . .	620,033	1,131,086	1,846,384	3,676,451
Perak . . . . .	94,848	272,804	383,073	1,060,543
Negri Sembilan . . . . .	146,891	586,864	963,253	1,346,499
Pahang . . . . .	...	...	...	...
Malacca . . . . .	12,000 <sup>3</sup>	23,490	52,980	36,865 <sup>4</sup>
Province Wellesley . . . . .	13,560 <sup>3</sup>	83,131	92,600	298,516
Johore . . . . .	47,724	182,495	201,632	327,635
Kelantan . . . . .	...	...	...	...
Total . . . . .	935,056	2,278,870	3,539,922	6,741,509

<sup>1</sup> *I.R.J.*, 1911, vol. xli. p. 103.

<sup>2</sup> Includes the Federated Malay States, Straits Settlements, Johore, etc.

<sup>3</sup> Approximate.

<sup>4</sup> This was the figures returned, but the actual output was probably higher.



FIG. 111. OLD STONE PLANTERS IN THE MAYA PENINSULA  
ORGANIC GARDENS (CONTINUED)



The exports from the Federated Malay States for 1910 compared with 1909 were as follow:<sup>1</sup>—

#### FEDERATED MALAY STATES EXPORTS

From	1910.	1909.	Increase.
Perak . . . . .	lb. 2,541,756 <sup>2</sup>	lb. 973,738	lb. 1,568,018
Selangor . . . . .	8,241,388 <sup>2</sup>	4,235,478	4,005,910
Negri Sembilan . . . . .	1,423,453 <sup>2</sup>	878,533	544,920
Pahang . . . . .	5,929	66	5,863
	12,212,526	6,087,815	6,124,711

The exports from the whole Malay Peninsula for the years 1908–10 have been as follow:—

#### MALAY PENINSULA

##### *Exports*

1908.	1909.	1910.
1575 tons.	3330 tons.	6504 tons.

Allowing for the rubber produced on the plantations of Ceylon (642 tons in the first half of 1910), Java, Sumatra, and Borneo, the total production of Eastern plantation rubber in 1910 must have been considerably over 8000 tons.

#### FUTURE PRODUCTION

Any forecast of future production necessarily involves a consideration of the two main factors—(a) the total acreage planted or to be planted, (b) the yield per acre. It does not

<sup>1</sup> *I.R.J.*, 1911, vol. xli. p. 430.

<sup>2</sup> The figures for Selangor include 72,171 lb. produced in Perak, and 1,158,236 lb. in Negri Sembilan.

appear to me that there are as yet sufficient data of an exact nature to enable one to make positive statements with any degree of assurance in regard to either of these factors.

It seems fairly certain, for instance, that in the Federated Malay States over 400,000 acres have been planted and cleared for rubber, and that a further 200,000 to 350,000 acres have been alienated. Whether the whole of the alienated area will be planted up, and if not, what proportion of it; or, again, whether further areas will be alienated and subsequently planted up,—all these are questions the answers to which depend on a number of complex factors—labour, demand for the raw material, financial considerations, etc.—the bearing of which cannot yet be determined.

### PLANTATION YIELDS

In regard to yield per acre—leaving out of consideration for the moment the possibilities of widespread disease and other natural calamities due to avoidable or unavoidable causes—the situation is also by no means as clear as might be desired. The first point to be considered is, what are the actual yields that are being obtained on favourably situated, good class estates?

The following figures (cf. *I.R.J.* 1910, vol. xxxix. p. 581) may be taken as a fair instance of present production in this connexion:—

Company.	Number of Trees or Acres Tapped (1909).	Total Crop (1909).	Yield per Tree or per Acre.
Lingga . . . . .	151,796 trees	lb. 545,219	lb. 3.58 per tree
Highlands and Lowlands . . .	1,220 acres	346,259	28.4 per acre
Con. Malay . . . . .	57,145 trees	215,893	3.78 per tree
Pataling . . . . .	60,000 trees (about)	152,090	2.53 per tree
Selangor . . . . .	924 acres	326,654	353 per acre
Damansara . . . . .	683 acres	202,440	296 per acre

From these figures it is obvious that at the present time first-class estates are producing from trees varying in age from 5 to about 13 years (mainly 5 to 10 years) at the rate of about 300 lb. to the acre, for it may be safely assumed that where the returns are per tree, that, on the average, not less than 100 trees to the acre have been tapped—probably many more. From my own observations in Malaya during the summer of 1910, I am satisfied that (on favourably situated estates) a production of 300 lb., and in some cases up to 400 lb. per acre, represents normal and not excessive tapping. The question whether, as the trees increase in age (after allowing for thinning out), an appreciably higher yield will be obtained is one that cannot yet be answered with any certainty. It is true that isolated trees or groups of trees, varying from 15 to 30 years in age, have in the experimental stations in Malaya and in Ceylon yielded up to 15 to 20 lb. per tree, but the yield per tree is frequently a misleading figure, and there are—as far as I am aware—no records of yields per acre *on the plantation and covering any extended area and time*, which can lead us to regard even as possible regular yields of say 800 to 1000 lb. per acre. I mention these figures because one not infrequently comes across statements to the effect that such yields are quite probable. Such statements are usually based on the fact that a particular area has actually produced such a quantity. I have myself seen on an estate in Malaya a plot covering a goodly number of acres which had produced over 800 lb. to the acre, but the absence of bark renewal was so marked that the manager of this particular estate determined to cut down fully half the trees. The latter had been planted  $8 \times 8$  (681 trees to the acre) and were seven years old. The yield, therefore, was little over 1 lb. per tree. While I do not deny that many estates may regularly produce 400 to 500 lb. per acre, I cannot say that the data at present available indicate with any certainty that more than 300 lb. can be relied upon generally for medium grade estates.

## TOTAL PRODUCTION IN 1916

In Malaya, although, of course, there is considerable variation according to the district, the conditions are, on the whole, very even, and taking good, bad and medium estates together, I believe it is fairly safe to prophesy an average yield of 220 lb. per acre in bearing, when the whole of the trees now under rubber have reached the producing stage—say in 1916. The result is that if the whole of the area in Malaya now under rubber is normally developed,<sup>1</sup> there would by that date be a production (400,000 acres at 220 lb., or one ton for ten acres) of about 40,000 tons. It must be remembered, next, that in addition to the area actually planted, there is, in the Malay Peninsula, a probable further area of 300,000 acres alienated for rubber. If we assume that one-quarter<sup>2</sup> of this will be planted up and brought into bearing, a further 10,000 tons, making 50,000 tons in all, will be available from the Peninsula in 1916. While conditions in the Malay are very even, the same cannot be said of Ceylon, and it is impossible therefore to forecast with any accuracy what the production there will be five or six years hence. At the present time Ceylon is producing roughly one-third to one-fourth as much rubber as Malaya, but although, judging by the planted acreage, this proportion should increase to the advantage of the island, it may be safer to assume that this will not be the case. On this basis Ceylon should produce about 12,000 tons at the date referred to.

No figures on which anything approaching to an accurate forecast for Java, Sumatra, Borneo and India can be based are available, but, taking the area planted in 1910 as 200,000 acres, and the rate of production as in the Malay, we get a further 20,000 tons to add to the total.

<sup>1</sup> I mean in the absence of any serious troubles in regard to labour, disease, etc.

<sup>2</sup> I have based this estimate on the figures referring to the ratio of planted to reserve areas exhibited by some of the older companies.



. YEAR OLD RUBBER TREES  
COTTA ESTATE, COFFEE



The figures, then, are as follow:—

PRODUCTION (ESTIMATED) OF EASTERN PLANTATIONS IN 1916

	Tons.
Malaya . . . . .	50,000
Ceylon . . . . .	12,000
Java, Sumatra, Borneo, and Southern India . . . . .	20,000
Total . . . . .	82,000

In the above no account has been taken of the plantations in the German Colonies (New Guinea, Cameroons, Africa) or Mexico, Brazil, and South and Central America generally. Probably, at a modest estimate, a further 10,000 tons from these areas may be relied on, giving a grand total of 92,000 tons.

As I have already mentioned, I have in making the above estimates not taken diseases or labour difficulties into consideration. These are matters which will be referred to subsequently (see pp. 91-94), but I may say here that while I do not anticipate that either of these causes will directly affect the production as estimated, it is quite likely that they may have a serious bearing on the cost of production, and so indirectly tend, in the long run, to reduce production—perhaps not a unmixed evil.

#### BASIC IDEA OF THE PLANTATION INDUSTRY

The basic idea underlying the plantation industry is that of producing under skilled white superintendence the maximum amount of high-class rubber on a limited area in a favourable and accessible region. The advantages and disadvantages of this system will be discussed later.

*Climate and Locality suitable for Planting*

Tropical and sub-tropical regions possessing a moist but equable climate, with no excessive temperature, heavy night dews and a moderate rainfall, are most suitable for rubber planting. For instance, in the planting districts of Malaya, where the conditions in this connexion are almost ideal, the maximum day temperature is roughly 85°-87° Fahr., the night temperature is in the vicinity of 77° to 79°, the rainfall about 80 to 120 inches, and the humidity 80-90 per cent. There are also regular and heavy night dews.

*Land*

Broadly speaking, land which is gently undulating and readily drained is most suitable. On hilly land the danger of "wash-outs" is considerable, but in other respects it possesses advantages, inasmuch as there is less drainage difficulty, and bark renewal is facilitated by the greater amount of available light. For *Hevea* a medium elevation, preferably not exceeding 1000 feet, is desirable, although in parts of Ceylon it has shown fairly satisfactory growth up to 3000 feet. Other species, for instance, *Manihot*, *Sapium* and *Guayule*, appear to do better at greater elevations, good results being obtained at altitudes of from 3000 to 5000 feet.

*Nature of Soil*

Compared with many other tropical products, rubber will flourish in comparatively poor soil. Thus *Manihot*, from many accounts, will thrive on poor rocky soils where nothing else but desert plants will grow, and will stand droughts (up to six months) which would be fatal to other species. Although some planters appear to express a predilection for a stiffish clayey soil, the balance of opinion seems to favour, as most suitable for rubber, a light to medium sandy loam. A highly important feature

is that the soil should be in a fine state of mechanical division.

According to Mr. Kelway Bamber,<sup>1</sup> the soils of Malaya may be classified into two main types—(a) alluvial pseudo-clays or muds (in the neighbourhood of the river and of the sea), (b) light sandy loams (inland and on the higher ground).

The following analyses are representative of these two types of soils:—

### ANALYSES OF MALAY SOILS (KELWAY BAMBER)<sup>1</sup>

#### A. Mechanical Composition

	Alluvial Clays.			Sandy Loams.		
	1. per cent.	Subsoil. 2. per cent.	3. per cent.	4. per cent.	5. per cent.	6. per cent.
Fine soil passing 90 mesh.	96.00	95.50	68.00	30.00	36.00	26.00
" 60 "	4.00	4.50	32.00	34.00	38.00	30.00
Medium " 30 "	...	...	...	26.00	8.00	22.00
Coarse sand and small stones	...	...	...	10.00	18.00	22.00

#### B. Chemical Composition

Moisture . . . .	6.920	5.560	5.000	1.400	4.000	2.200
Organic matter and combined water . . . .	24.080	16.640	8.000	3.000	9.600	5.600
Oxide of iron and manganese . . . .	1.120	1.000	3.000	0.300	8.240	0.700
Oxide of alumina . . . .	2.971	3.019	2.520	1.165	4.183	2.516
Lime . . . .	0.284	0.200	0.160	0.140	0.160	0.160
Magnesia . . . .	0.252	0.381	0.230	0.130	0.100	0.130
Potash . . . .	0.131	0.169	0.014	0.014	0.053	0.030
Phosphoric acid . . . .	0.025	0.012	0.076	0.051	0.064	0.064
Sand and silicates . . . .	64.200	72.800	81.000	93.800	73.600	88.600
Chlorine . . . .	0.017	0.019	...	...	...	...
	100.000	100.000	100.000	100.000	100.000	100.000
Containing nitrogen . . . .	0.667	0.425	0.403	0.492	0.386	0.403
Equal to ammonia . . . .	0.810	0.516	0.489	0.598	0.469	0.489
Lower oxide of iron . . . .	much	fair	good	good	good	good
Acidity . . . .	...	...	marked	marked	marked	marked

<sup>1</sup> Report published by the late J. B. Carruthers. Cf. Wright, *Hevea Brasiliensis*, 3rd ed. p. 59.

<sup>2</sup> Wright, *loc. cit.*

Although they show considerable variation, the above soils are obviously well provided with nitrogen, but by no means over-rich in phosphoric acid and potash; indeed, in Nos. 3 and 4 the potash, and in Nos. 1 and 2 the phosphoric acid, are decidedly low. As regards mechanical subdivision, the pseudo-clays are evidently superior to the sandy loams.

I have already referred to the fact that, on the whole, the planting districts of Malaya show a remarkable evenness of climate and soil, but the analyses recorded above (and many similar ones published elsewhere),<sup>1</sup> nevertheless, indicate that there is a certain amount of patchiness. I had occasion during a recent visit to Malaya to observe this patchiness, and also the fact that some planters and planting companies do not appear to have realized it, or to have had any soil examinations carried out previous to planting. Where planting on these poor soils has taken place, and I have, more particularly in Johore, seen plantations on excellent soil, and almost within a stone's throw of these, hundreds of acres of trees starved and weakly through absence of soil nourishment, a system of rational manuring is obviously indicated, and might be carried out on a considerably wider scale than has yet been attempted. I may in passing remark that although, broadly speaking, nitrogen in a manure increases vegetative growth and potash develops wood, it does not always follow that lack of development in either of these directions necessarily implies an absence of either of the constituents referred to. In every case all the circumstances and the constitution of the soil generally must be taken into consideration.

The following figures relating to rubber soils analysed in my laboratory may be of some interest as affording a comparison between typical Malay soils and those in other parts of the world:—

<sup>1</sup> Wright, *Hevea Brasiliensis*, 3rd ed. chap. v., in which a considerable number of soil analyses from different planting districts are recorded.



A VIEW OVER PART OF BUKIT RAJAH, TAKEN FROM THE HILL.



## (a) SUMATRA SOIL

Analysis by the Author

	Mechanical Analysis Per cent.
Passing 90 mesh . . . . .	. 5.7
" 60 " . . . . .	. 5.7
" 30 " . . . . .	. 26.5
Coarse sand and gravel . . . . .	. 62.1
	Chemical Analysis.
Moisture . . . . .	. 25.03
Organic matter and combined water . . . . .	. 5.12
Lime . . . . .	. trace
Carbonates . . . . .	. nil
Iron . . . . .	. much
Potash (soluble in HCl) . . . . .	. 0.26
" (citric soluble) . . . . .	. 0.016
Phosphoric acid (soluble in HCl) . . . . .	. 0.072
" " (citric soluble) . . . . .	. 0.010
Nitrogen . . . . .	. 0.27
" =ammonia . . . . .	. 0.33
Acidity . . . . .	. faint

## (b) WEST AFRICAN SOIL

Analysis by the Author

	Mechanical Analysis. Per cent.
Passing 90 mesh . . . . .	. 14
" 60 " . . . . .	. 4
" 30 " . . . . .	. 8
Coarse sand and stones, etc.. . . . .	. 60
	Chemical Analysis.
Moisture . . . . .	. 11.6
Organic matter and combined water . . . . .	. 6.75
Nitrogen . . . . .	. 0.20
" =ammonia . . . . .	. 0.24
Phosphoric acid (soluble in HCl) . . . . .	. 0.35
" " (citric soluble) . . . . .	. 0.011
Potash . . . . .	. 0.37
Sand and silicates . . . . .	. 79.20
Acidity . . . . .	. faintly acid

It will be noticed that soils (a) and (b) compare not unfavourably with the Malay soils in regard to potash and phosphoric acid, but they contain less nitrogen and are not

so satisfactory from the point of view of mechanical composition.

(c) UGANDA SOILS FROM THE MABIRA FOREST

Analyses by the Author

	1. Red earth from forest. Typical <i>Funtumia elastica</i> soil.	2. Black earth from lower levels of forest in which <i>Funtumia elastica</i> occasionally thrives.
		Mechanical Analysis.
Fine soil passing 90 mesh . . . . .	Per cent.	Per cent.
" " 60 " . . . . .	9.71	3.87
" " 30 " . . . . .	6.86	3.85
Coarse sand and stones . . . . .	17.14	9.23
	66.29	83.05
		Chemical Analysis.
Moisture . . . . .	2.66	5.58
Organic matter and combined water . . . . .	14.42	10.38
Nitrogen . . . . .	0.317	0.975
" as ammonia . . . . .	0.284	1.140
Phosphoric acid (soluble in HCl) . . . . .	0.15	0.325
" (citric soluble) . . . . .	0.012	0.088
Potash . . . . .	0.19	0.18
Sand and silicates . . . . .	64.92	56.47
Lime, iron, and alumina . . . . .	17.66	17.07
Iron . . . . .	large amounts strongly acid absent	
Acidity . . . . .	faintly acid absent	
Carbonates . . . . .		

The state of mechanical subdivision of the typical *Funtumia* soils is interesting, and appears to indicate that this species will stand a longer drought than *Hevea*—that is if the current theories regarding the value of finely divided soils for the purpose of growing the latter species are well founded.

#### PLANTATION METHODS

I have no intention of attempting to say all that there is to be said about planting and plantation methods, in the first place because there are many others better qualified for this task than I am, and secondly because so much of

it has been fully and well said elsewhere.<sup>1</sup> Nevertheless, I venture to believe that a brief and connected account of plantation methods as they appeared to me during the course of a tour through the Middle-East in the summer of 1910, may not be without interest to those who desire to obtain some practical idea of the rubber industry as a whole, and also of the latest views held on the spot regarding various more or less controversial questions.

### *Clearing*

If—as is generally the case—the ground acquired consists of virgin jungle, it must, before any of the planting operations proper can be thought of, be thoroughly cleared. The first operation is that of cutting down the undergrowth, and then the timber. Before the next step—that of burning—can be taken, the undergrowth must be thoroughly withered, or an unsatisfactory “burn” will result. It frequently happens that the rains prevent burning off for weeks at a time, and there is perhaps nothing that tries the planter’s patience so much as this. It is generally admitted that after “burning” sufficient time should be allowed to elapse for all the tree stumps, pieces of loose timber, and, in fact, everything of the nature of decaying vegetable matter, to be destroyed and absorbed by the soil before planting commences. Decaying vegetable matter may give rise to all kinds of trouble in the guise of diseases and pests, but in the hurry and scramble of the recent “boom” the good rule regarding the waiting period after the “burn” appears to have been frequently neglected. It is now generally held that the best plan to prevent the spread of root and other diseases is to remove the whole of the unburnt timber, notwithstanding the fact that this involves considerable expense.

<sup>1</sup> Cf. Wright, *Hevea Brasiliensis*, 3rd ed. (London : Maclaren & Sons, 1908) ; W. H. Johnson, *Para Rubber* (London : Crosby Lockwood, 1909) ; and *Lectures on Rubber*, edited by D. Spence (London, 1909), etc.

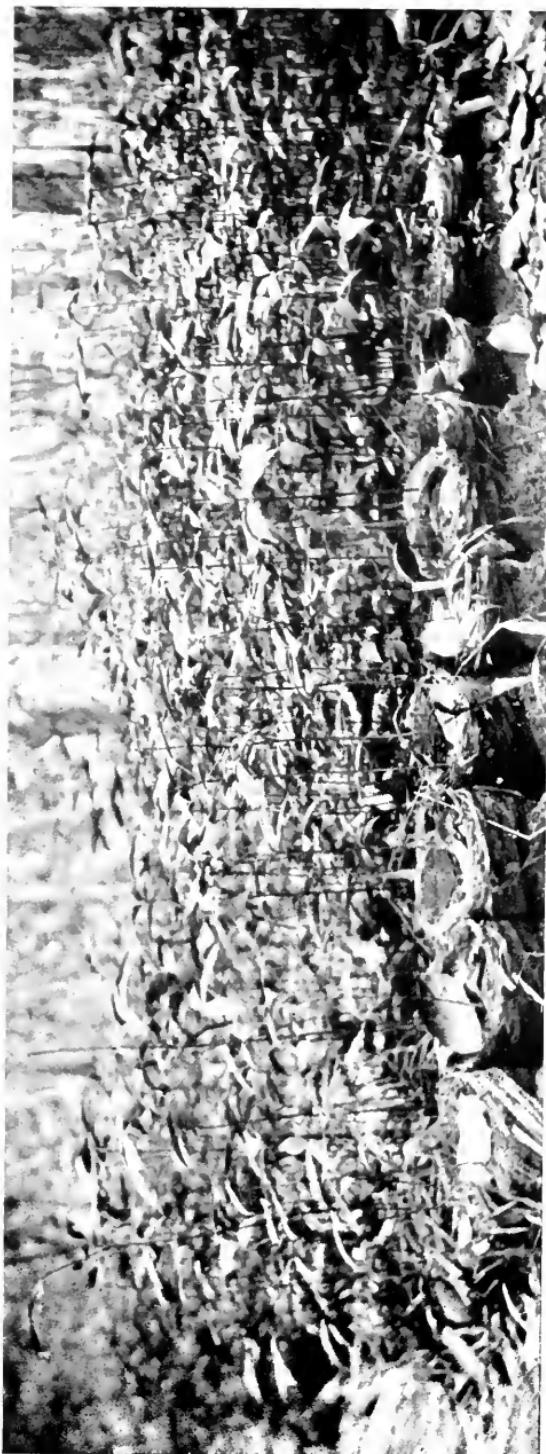
*Lining and Holing*

After the land has recovered from the "burn," the lines along which the trees are to be planted are marked out, and holes (generally about 18 inches deep by 12 inches diameter) dug to receive the young plants at the proper intervals. Previous to this, naturally, a decision must have been taken regarding the number of trees to the acre to be planted, and the method of spacing determined.

*Spacing*

One of the most important planting questions, and one that has not yet been satisfactorily settled, is that of spacing. Put in a nutshell, the question is how many trees shall be planted to the acre. In the early days of the planting industry it was generally considered that fairly close planting gave the best results, that is to say, the highest yield per acre, but wider experience has shown that although closely planted rubber may give a high yield at an early period, this yield will rapidly fall off, mainly because the absence of light is fatal to the proper renewal of bark. It is obvious also that the soil can only give up as much plant nourishment to 500 trees on an acre as to 100 trees planted on the same space, at any rate after a certain period of growth has passed. The closest planting that I have seen is 8 by 8 feet, and this corresponds to 681 trees to the acre. I have already referred to the fact, however, that when the trees planted in this way had reached an age of 7 years it was decided to cut down fully one-half of them. Whether a yield of 800 lb. to the acre which was obtained from the closely planted trees in question will be obtained from one-half the number of trees on the same area is very questionable, but, on the other hand, it is fairly certain that if the trees had not been thinned out the yield would eventually have fallen off to a very small figure indeed. At the present time planting is being done at distances varying from 12 by 12 feet (300 trees per acre) to 20 by 20 feet (110 trees per acre),





HEVEA SEEDLINGS IN BASKETS (SEE PL. 55)  
(THE NURSERY IS PROTECTED BY THE SHADE OF 7-YEAR OLD TREES)

but as the branches of trees planted 40 feet apart have been known to touch at an age of 10 years, it is still doubtful whether 20 by 20 feet represents sufficiently wide spacing. In the past much land has been planted fairly closely with the idea of thinning out at a later period, and so getting the benefit of the large early yield as well as the subsequent benefits accruing from wide spacing. This thinning out process is, however, not so easy to carry through as one might at first imagine. To begin with, the *Hevea* shows such vitality that it is not easy to bleed it to death, and to cut down a healthy latex-yielding tree appears from sentimental and practical reasons not to be a very rational proceeding. Moreover, the complete removal of the stump of the cut down tree is liable to give rise to trouble and is expensive.

There are other points which require consideration in connexion with the question of spacing. If the local considerations make the interplanting of catch crops or permanent crops necessary or desirable, fairly wide planting is obviously a desideratum. Generally speaking, close planting is productive of tall, spindly trees, wide planting of sturdy, well formed trees. This in itself is a considerable advantage, as a greater surface of readily accessible bark is exposed for tapping.

#### *Propagation*

The young plants are raised from seed, generally in baskets or pots. Occasionally the direct planting of seed is resorted to.<sup>1</sup> A variety of methods obtain for the rearing of the young plants. In some cases the nursery has for shelter merely the protection of older trees (see Plate VIII.); in others a roof or open shed is employed. I have also seen very young trees in the open forming a nursery without

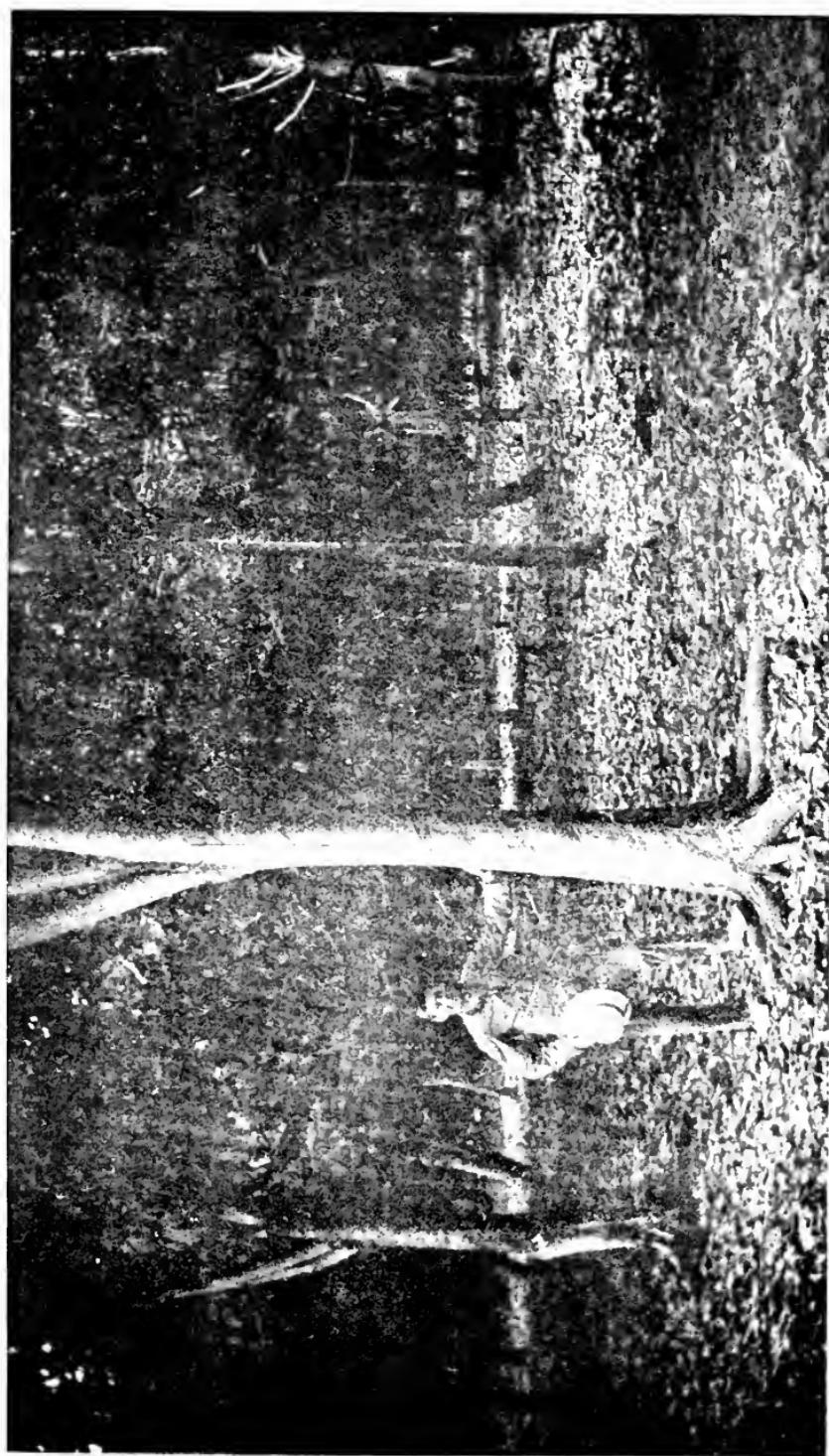
<sup>1</sup> In Ceylon (according to a private communication from Mr. Herbert Wright) quite a number of estates, including some of the best, have been raised from seed at stake. It is a method, however, which can only be adopted when planting weather coincides with the harvesting of the seed crop.

any protection at all. Nursery methods will necessarily vary according to the district and general nature of the land. Where heavy winds may be expected or where wash-outs are likely to occur, more protection is obviously required than in districts where these conditions are improbable.

*Seedlings and Stumps.*—There are two main methods of developing the young plant. It is either planted as a seedling at stake or it is placed in its final location in the form of a "stump." The stump is merely a seedling at a somewhat later stage of development, which has been trimmed so as to remove the lower vegetative parts. Both seedlings and stumps have advantages and disadvantages, but I gathered in Malaya that the general consensus of opinion is to the effect that seedlings are preferable, and that, generally speaking, better results are obtained from them. The advantage of the seedling is that it can be transported bodily from the nursery, and that it gives a tree of normal growth. The stump is inclined to produce tall, spindly trees, and, on account of the hacking to which it has been subjected, is more liable to be attacked by diseases and pests than the seedling. In many cases seedlings are not available, or the season may be against their planting, and in such cases, of course, the stump must be employed. Stumps can be readily transported over considerable distances, and may, therefore, be obtained as required. The advantage of the stump is that, as vegetative growth starts from the very top the plant is not so liable to be attacked by rats and other small animals which are inclined to make a feast of the tender shoots of the lower parts of the seedling.

#### *Weeding*

There is no subject in connexion with planting, if we except that of spacing, which has led to so much discussion as the question of clean weeding. These discussions appear to me, however, at the present day to be mainly academical, and to be carried on by those who are scarcely familiar with the present-day practical aspects of the question. From



YEAR OLD HEAT ON A SPANISH FERN  
CULTIVATED AND PLANTED IN THE AMERICAN WOODS



what one sees in print on this subject, one would gather that there is still a considerable difference of opinion as to whether clean weeding or interplanting, whether protective or productive, is the better method. I may say that I did not come across a single planter in Johore, Selangor, Perak, or Province Wellesley who had any doubt whatever on the point. Every one agreed that where it was possible to clean weed this was far and away the best method. In the Klang district it is indeed the exception to see any plantation of note that is not clean weeded, but in other districts, for various reasons, interplanting is more resorted to. Those who are not familiar with this question may want to know why clean weeding is not everywhere carried out. The answer to this is simple, and it is that on some plantations clean weeding is impossible owing to the shortage of ordinary coolie labour, and on other plantations, as a result of bad management, the undergrowth has so far obtained the upper hand that clean weeding is almost out of the question, for in these cases the cost of clean weeding may be anything from 30 to 60 dollars per acre. The reason why clean weeding is desirable is that the object of every planter is, or should be, to obtain the maximum amount of rubber in the shortest possible time, consonant with the avoidance of injury to the trees. All weeds, and naturally also any intercrop, obviously require a certain amount of plant food, and in proportion as the food-stuffs required by the weeds or intercrop are greater or smaller the growth of the rubber tree is affected. The ideal intercrop is one which, while preventing the development of weeds, will give a return which is greater than the loss due to the relatively slower growth of the rubber tree. Such an intercrop has yet to be found, at any rate, as long as rubber prices remain high. In districts in which clean weeding is impracticable on account of shortage of ordinary coolie labour, a system of leasing the land between the rubber trees to local farmers has been developed. The farmers keep the land clear, and plant such crops as

tapioca, indigo, coffee, etc., as the case may be. The produce, of course, reverts to them, the sole advantage to the planter being that the farmer undertakes to keep the land clear of weeds and undergrowth. Where this system prevails, or where, for some other reason, an intercrop is necessary, indigo or robusta coffee are perhaps the most satisfactory in making the least demand on the soil. In some districts one sees a good deal of tapioca interplanted, but planters appear to be coming to the conclusion that this crop is too heavy for the soil.

### *Protective Interplanting*

While, as I have already said, clean weeding is now generally found to be desirable wherever it can be applied, there is one condition under which it may yet in the long run be necessary to depart from the general practice. This is on sloping ground, where the danger of wash-outs is considerable, particularly in the case of younger growths. It yet remains to be determined, however, which is the most favourable undergrowth for protective purposes. Thus, *Passiflora*, which has been somewhat extensively tried, does not seem to be a success. It was believed that this creeper would keep down the lalang, but I have seen numerous patches of *Passiflora* through which the lalang gaily makes its way (see Plate XI.). While clean weeding is now the favourite method, and is applied—at any rate in Malaya—wherever practicable, it must not be forgotten that the planting of a single (and non-indigenous) species over extensive areas of recently cleared jungle is not without potential danger of a serious nature. Experience has shown that diseases and pests are more likely to make headway and to assume epidemic form under the conditions referred to, than is the case where a variety of trees or plants are present. In the jungle the *Hevea* is peculiarly immune from the attacks of insects and micro-organisms, the reason apparently being that they prefer other forms of vegetation. When, however, they are deprived of the means of nourish-



RUBBER AND INDIGO (PROV. WELLESLEY)



RUBBER AND TAPIOCA (PROV. WELLESLEY)



ment most suitable to them, they necessarily turn their attention to that which remains available. It has been suggested that the most suitable and natural method of preventing insect and pest epidemics is to have a fairly extensive jungle belt in the immediate neighbourhood of the plantation, or preferably to have the plantations separated from one another by jungle belts, but the immediate application of these principles would involve considerable practical difficulties at the present day, although, in time, they might well be carried out.

### *Tapping*

In the vast majority of rubber-bearing species the rubber is present in the form of an emulsion termed *latex*. The latex is contained in a special cell system (which must not be confused with the system containing the tree "saps") termed the laticiferous system, situated between the outer bark and the cambium. The structure of this system varies considerably according to the species, and this fact has an important practical bearing on the method of tapping to be employed. In the case of some species the removal of a relatively small area of bark is sufficient for the purpose of collecting substantially all the latex obtainable from the tree over a relatively lengthy period of time. Two to six tappings per annum, for example, will give as good or better a yield than a greater number of tappings. This is the case, for instance, with *Funtumia elastica*, and also, apparently, with *Castilloa elastica*. *A priori*, one would imagine that species which behave in this manner would possess a decided practical advantage over *Hevea*, which only yields its latex very gradually and therefore requires a large number—100 to 150 may be considered a fair minimum—of tappings to produce its maximum. Experience has shown, however, that the *Hevea* in regard to regularity and quantity of output easily surpasses the others. Possibly this may be accounted for by the fact that the *Hevea* is the only one of the more important rubber trees which exhibits

the remarkable phenomenon of "wound response" to any marked degree. The first tappings of *Hevea* always give poor results, but the yield gradually increases up to a maximum as the process is repeated. This fact has long been known to the native collectors of the Amazon district, where the practice is to make a number of single cuts well above the ordinary tapping level on the day preceding the commencement of the tapping operations proper.

### *Tapping Age*

It is generally admitted that it is unwise to tap an immature tree, firstly, because the young tree is more easily injured than older growths, and, secondly, because the quality of the rubber is poor. Opinions differ, however, in regard to the age at which a tree is mature, or rather, tappable. Such opinions are, perhaps, not always entirely uninfluenced by immediate (if short-sighted) commercial considerations. In some districts growth is far more rapid than in others. Thus in Malaya, speaking broadly, a 4 year old tree will be in point of development as far advanced as a 5 to 6 year old growth in Ceylon. I have heard of the tapping of 3 year old trees, reputedly with success, in Malaya, but notwithstanding this I do not think that in placing the minimum age at which *Hevea* should be tapped, even in the most favoured districts, at 4 to 5 years, that I shall meet with any serious criticism.

### *Tapping Seasons*

In the chief plantation districts<sup>1</sup> there is very little seasonal variation, and, practically speaking, the trees may be tapped all the year round. In this regard the plantations are at an advantage as compared with the Amazon, where, mainly on account of the flooding of the low-lying

<sup>1</sup> This applies, more particularly, to Malaya and parts of Java, Sumatra, and Borneo. In Ceylon and East Java there are marked seasons. Occasionally (e.g. during the year of writing) there is some evidence of considerable climatic periodicity in Malaya.



A

EXPERIMENTAL PROTECTIVE PLANTING OF PASSIFLORA AMONG HEVEA  
ON A SELANGOR ESTATE. THE LALANG COMES THROUGH AND GROWTH  
OF RUBBER IS RESTRICTED. (SEE P. 52)



B

PART OF THE SAME PLOT AS ABOVE, BUT THE PASSIFLORA CREEPER  
IS SHOWN FORKED UP. THE GROWTH OF THE RUBBER IMPROVED QUITE  
25 PER CENT. AFTER FORKING. (SEE P. 58)



districts from which the bulk of the rubber is collected, work is only possible during six months in the year.

### *Tapping Methods*

The modern practice is to tap the trees to only a moderate height, say 6 to 10 feet for ages from 5 to 12 years. High tapping produces latex poor in rubber content and also tends to cause the tree to run dry. With regard to the kind of tapping instrument in general use, innumerable "patent" tapping knives have been devised, mostly with adjustable blades. The inherent defect in this kind of knife is that the native tapper is very prone to alter the adjustment according to his fancy, frequently with disastrous results to the trees. In the Selangor district of the Federated Malay States I found a general consensus of opinion that "patent" knives are anathema, and that the ordinary gouge is the most suitable instrument. Two species of gouges are employed, namely, the plain gouge and the wry-necked gouge. It is held by experienced planters that the plain gouge is the best instrument, but requires more skill, and the general practice seemed to me to be to allow the well trained coolie to employ the plain gouge and the relatively new hand the other variety. In districts other than Selangor I occasionally saw a "patent" knife in use, but the impression produced on me was that on the whole they are very little employed. Fig. 1, p. 62, represents in diagrammatic form the principal methods which are or have been used for tapping. *V tapping (a)*, which is a usual form on the Amazon, has been almost entirely abandoned on the plantations. As is also the case in system *e* (spiral) a considerable number of cups are required, whereas the remaining systems require no more than one spout and one collecting vessel. Systems *b* (*full herring-bone*) and *e* (*whole or half spiral*) are also rarely employed nowadays, mainly because they involve excessive bark removal and weakening of the tree. Of late the *basal V* system (*d*) has come into some favour in certain districts, but far and away the most

widely employed method is that of the *half herring-bone*, and particularly that variety thereof which is known as the *4-quarter* system. Opinion is still divided as to whether it

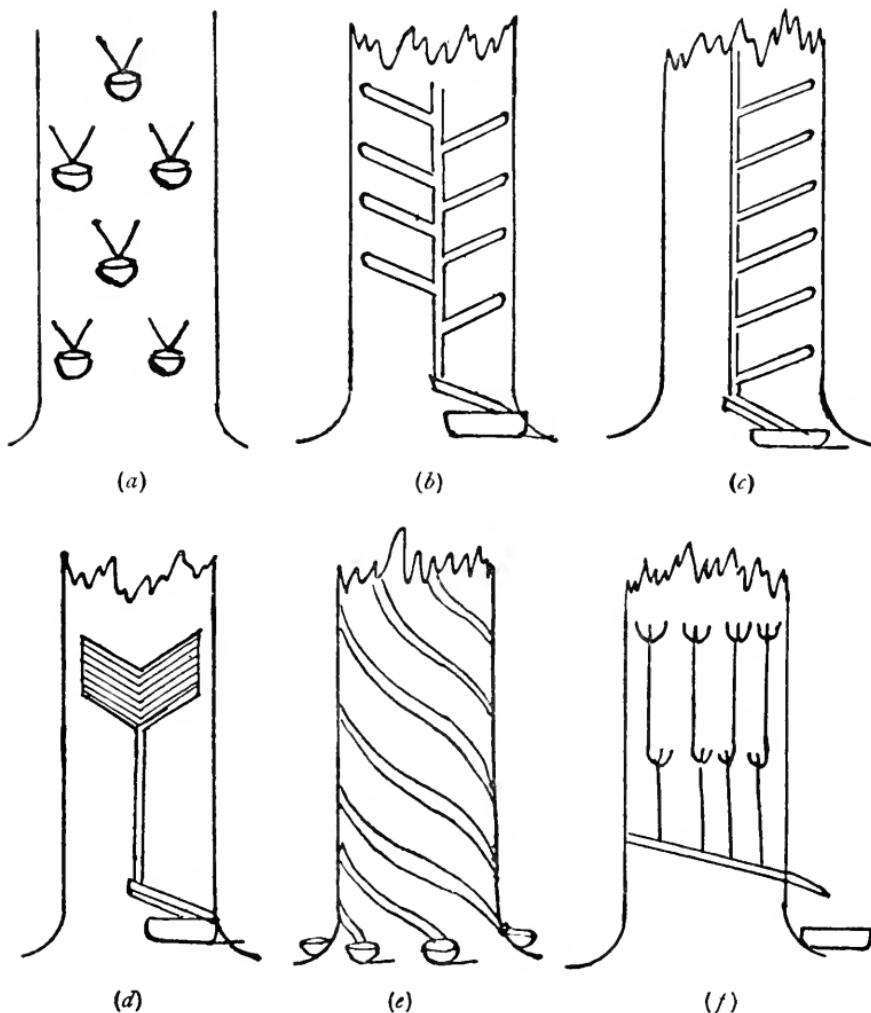
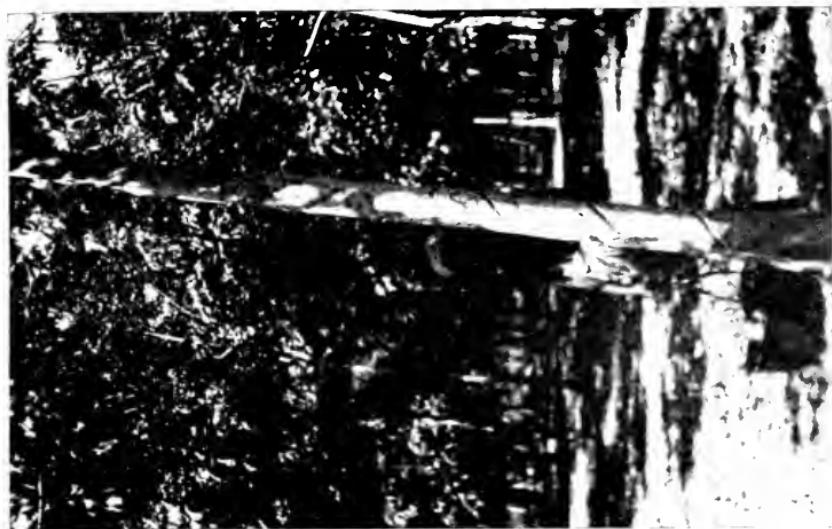
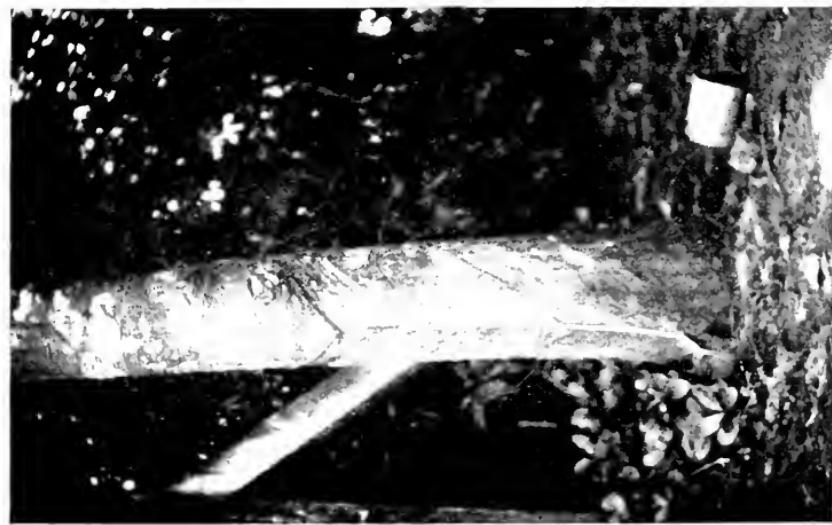


FIG. 1.—Diagrammatic Representation of Tapping Methods  
 (a) V tapping; (b) Full herring-bone; (c) Half herring-bone; (d) Basal V;  
 (e) Spiral; (f) New Northway.

is best to work only one or two quarters in the year, and whether the successively tapped quarters should be opposite or adjacent, but I am inclined to think that the balance



1 YEAR OLD HEVEA ON A SELANGOR PLANTATION



7 YEAR OLD HEVEA (PROVINCE WELLESLEY)  
SHOWING FLOW OF LATEEN IMMEDIATELY AFTER TYPHOOON



of opinion will definitely veer in favour of one quarter per annum and opposite quarters in succession. System *f* has recently been advocated by Mr. Northway, but it is as yet early to say whether it will prove to be of a practical nature. After the tapping design has been marked on the tree, the central channel (*e.g.* in the herring-bone or basal V systems) is cut, and then a narrow strip (say 20 to the inch) of bark is pared away along the side marks. This process is repeated (generally daily or on alternate days) until the maximum of bark that can be safely removed has been cut. The "pricker," an instrument similar in appearance to the rowel of a spur mounted on a handle, which was used alternately or in conjunction with the knife with a view to stimulating wound response, or to reopening the line of a cut without any further material removal of bark, appears to have been generally discarded in Malaya; certainly I did not see one in use, nor hear anything to lead me to believe that it was still being employed to any extent. The same applies to the "drip tin," a vessel fixed to the tree above the line of latex flow containing water or dilute ammonia, and provided with a suitable device to permit of a slow dripping of the fluid into the channels, with a view to preventing the coagulation of and to promoting a regular flow of the latex. Experience has shown that in the case of *Hevea*, the latex of which flows with freedom, the advantages of the "drip tin" are outweighed by its disadvantages. For *Manihot*,<sup>1</sup> which (like *Ficus elastica*) has a marked tendency to coagulate along the tapping lines, it appears that the drip tin may be used with advantage.

#### PLANTATION YIELDS

Some facts have already been adduced (see p. 44) regarding the general yield per acre and, in individual cases, the yield per tree on the plantations, and it has been mentioned that, from a purely commercial point of view, the yield

<sup>1</sup> Cf. Preuss, *I.R.J.*, Quarter-Century Number, 1909, p. 80.

per tree is likely to prove misleading. It is, however, of interest to know what the average yield from trees planted on reasonable lines is likely to be, and I therefore give the following figures, which, according to my estimation, fairly represent what may be expected under average Eastern conditions:—

PLANTATION YIELDS PER TREE (*HEVEA*): ESTIMATED

5 years . . .	$\frac{1}{2}$ lb. to $\frac{3}{4}$ lb.	6 years . . .	$\frac{3}{4}$ lb. to 1 lb.
7 , , ,	$1\frac{1}{4}$ lb. to $1\frac{1}{2}$ lb.	9 , , ,	2 lb. to $2\frac{1}{2}$ lb.
12 years . . .	.	3 lb. to 4 lb.	.

I admit that the yield varies widely according to the district, soil, etc., and that in many cases far larger yields than these have been obtained.

#### COLLECTION OF LATEX

The latex is collected in cups or "tins" made of metal, glass or china. Cocoa-nut husks are also employed to some extent. I have not the slightest hesitation in saying that bare "tin" cups and cocoa-nut husks should be discarded. Latex should not be collected in any vessel the surface of which is liable to corrosion or to be affected either by the weather or by the latex itself. It is, moreover, very difficult to keep the interior of any cup not possessing a smooth, even, hard surface clean. The importance of cleanliness cannot be exaggerated. Normal latex collected in a cleanly fashion and with avoidance of metallic contamination is almost bound to give good results, provided, of course, that no serious error is committed in the subsequent operations. Metallic (iron) contamination affects the colour of the rubber obtained in some cases more than in others, but in addition to this, rust harbours dirt, and dirt leads to discolouration, tackiness, and other undesirable results. On the whole, I think glass is the most satisfactory material, and the loss from breakage does not seem to be very serious. I have no doubt that my views regarding cocoa-nut husks as collecting vessels will be criticized, for quite a number of plantation managers regard them with

favour, but in anticipation of such criticism I venture to suggest that where their use has not had any (apparently) marked detrimental effect, this is due to chance and not to any inherent virtue possessed by them.

### *The Avoidance of Premature Coagulation*

In order to prevent as far as possible premature or partial clotting or coagulation before the latex reaches the factory, it is customary to place a small quantity of water, and occasionally very dilute ammonia or formalin solution, in the cups. The dilution of *Hevea* latex tends to prevent coagulation, but it is necessary to add that this is not the case with all latices. The water used for the cups should be as clean as possible. Coloured or turbid water, or water containing much organic matter, may have a very decided effect on the quality of the rubber, particularly in regard to colour. I do not think that the use of either ammonia or formalin is desirable. Certainly they are both very efficient in regard to the prevention of premature coagulation, but there is much reason to believe that they affect the quality of the rubber. As far as my own experience in this connexion goes, I have noticed that latices to which ammonia has been added tend to produce rubber inclining to weakness and tackiness, whereas formalized latices (particularly in the case of *Funtumia*<sup>1</sup>) yield strong but rather harsh and somewhat inelastic products.

### *Formation of "Scrap"*

The clots of rubber which form in the cups and in the bulk collection vessels during transport to the factories, that is, prior to the straining of the latex in the latter, are handled separately from the main coagulum, and form the so-called "scrap." Now, as this "scrap" forms prior to straining, it is obvious that it will contain a considerable proportion of the impurities (small pieces of bark, leaves, mud splashed up by the rain, etc.) which would, if the latex could be kept absolutely fluid,

<sup>1</sup> Cf. Schidrowitz and Kaye, *J.S.C.I.*, 1909, vol. xxviii. p. 1264, and Christy, *I.R.J.*, 1909, vol. xxxvii. p. 400.

be entirely removed by the straining process. It seems to me, therefore, that next to the prevention of its formation—which is, apparently, impracticable—the most important point in connexion with the scrap problem is to obtain it in the purest possible condition, and that this result can be best achieved by straining the latex as soon as possible, that is, when the minimum of scrap has formed. With this end in view I have already suggested<sup>1</sup> elsewhere that it might be worth while to try straining in the field. This does not seem to me to be at all impracticable, and the cost of providing a strainer on wheels at each sub-station would be very small.

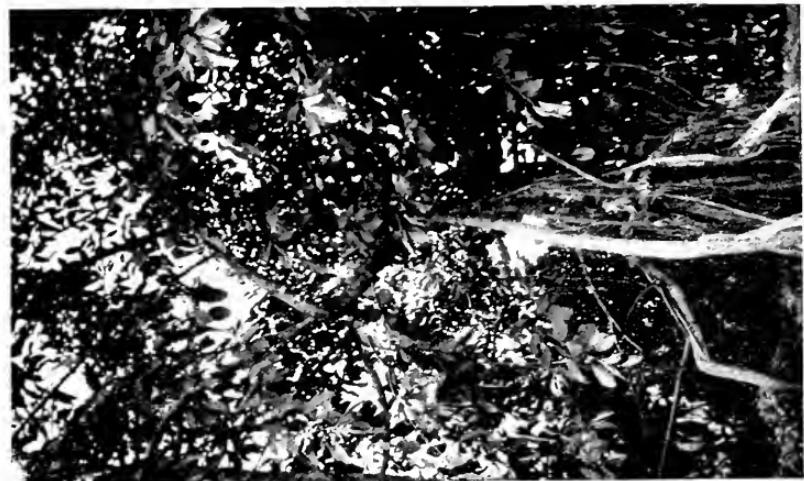
### *Coagulation of Hevea Plantation Latex<sup>2</sup>*

The trees are generally tapped in the early morning (roughly from sunrise to 10 a.m.), and, after the latex has been collected, it is transferred as quickly as possible to the factory. On some estates the whole or part of the trees are tapped in the afternoon and early evening, but the disadvantage of this method is that it is impossible to get the whole of the latex (at any rate from outlying stations) to the factory until the following day. The result is that an appreciably higher proportion of "scrap" is formed, and the delay in straining does not make for an improvement in the quality of the rubber.

Although numerous other methods have been suggested and tried, it is the fact that at the present time probably 99 $\frac{1}{4}$  per cent. of all plantation rubber is coagulated with acetic acid. It is yet too early to say definitely that this is the most suitable method from every point of view; on the contrary, I am inclined to believe that ultimately some, possibly radical, modification of the present system will have to be introduced, but for all practical purposes a description of the plantation coagulation method *as it is* begins and ends with acetic acid.

<sup>1</sup> Cf. *I.R.J.*, 1910, vol. xl. p. 679.

<sup>2</sup> For the theory of and further details regarding coagulation, see Chap. VIII.



*HEVEA BRASILIENSIS* (RAMBONG)

THE INDIGENOUS RUBBER TREE OF THE EAST. (See Fig. 102.)



*HEVEA BRASILIENSIS* (SELANGOR)

A  
13-YEAR OLD HEVEA (SELANGOR)  
EXPERIMENTAL HIGH PLANTING, THE LOWER PART  
SHOWS THE ORIGINAL FRESH COLES WITH FRESHLY  
PARK



After the latex has been strained in order to remove "scrap" and dirt, it is ready for the addition of the coagulant. It has been suggested that in order to achieve homogeneous results the latex should always be diluted down to a certain rubber content, but admirable as this suggestion is in theory, it does not always work well in practice, for the simple reason that, owing to the frequent rains (in Malaya, Java, Borneo, etc.) and the necessity of partially filling the collecting cups with water, the plantation manager as often as not has to deal with latex which is too watery rather than the reverse.

The acetic acid is added to the strained latex, which is then poured into the coagulating vessels. Where rubber of sheet type is made these vessels are generally of enamelled iron, 30 to 40 inches in length by 12 to 14 inches in breadth and 2 to 4 inches deep. "Biscuits," which are obtained by pouring the latex into shallow circular vessels, are rarely made in Malaya, but still to some extent in Ceylon. After a certain time, which varies somewhat, according to the quality of the latex, a clot shaped according to the containing vessel forms, and, if the conditions have been properly gauged, the "serum" or fluid remaining should be no longer milky in appearance, but clear and free from rubber.

Where only crêpe is made there is no need to pour the latex after the coagulant has been added into special vessels, but it may remain in the original bulk (enamelled iron or preferably earthenware) containers until setting has taken place. In certain cases, *e.g.*, where the rubber is allowed to get rather hard, that is where it is not washed and rolled within a short time of complete coagulation, but is (after having been removed from the serum and placed in clear water) allowed to "harden" for say twenty-four hours, it might, in my opinion, be advantageous to employ setting tins similar to those used for sheet, as the subsequent work of rolling to an even length of crêpe is thereby much facilitated. I am doubtful whether this process of preliminary

hardening is of any advantage. When the rubber clot first forms in the latex it is quite soft and cheesy. After a time—particularly if the liquor is replaced by clean water—a gradual hardening takes place. Now, the harder the rubber, the more difficult the washing operation becomes and the more the nerve of the rubber is affected thereby. Again, the soft freshly formed clot immediately hardens when rolled,<sup>1</sup> and this process of hardening by rolling may be accentuated by passing the rubber through a “sheeter” (even speed smooth rolls) after washing. Where rubber of a very light colour is required, the preliminary setting in a large volume of clean water is probably an advantage, as the removal of the enzyme or enzymes (ferments) which are responsible for the darkening of the rubber is probably accomplished more satisfactorily by this than by any other method. The ideal plan would be to wash in running water for a prolonged period, but this is rarely possible.

*The use and abuse of Acetic Acid.*—The process of coagulation by means of acetic acid was introduced by Mr. John Parkin<sup>2</sup> in Ceylon in 1898–99, and according to him the Peradeniya experiments showed that an appropriate quantity for the material worked on was 1 volume of pure acetic acid for 100 volumes of latex. This seems to me to be rather a high proportion, but it is the fact that latices vary very considerably in regard to the quantity of acid required. The quantity required will depend on the alkalinity—fresh *Hevea* latex is slightly alkaline—or relative acidity of the latex, on the rubber content, and finally on the general chemical and physical properties of the latex. The latter are of a decidedly complex nature, and will be dealt with in another chapter,<sup>3</sup> but it is quite evident from a consideration of the facts known to us that there is as yet no simple theoretical basis according to which the most appropriate quantity of acid for any given latex can be determined with ease and accuracy. It

<sup>1</sup> See p. 126 for an explanation of this phenomenon.

<sup>2</sup> Cf. *I.R.J.*, 1910, vol. xl. p. 752.

<sup>3</sup> See p. 116.

is from a practical point of view almost unavoidable that the quantity of acid should be sufficiently large to ensure complete coagulation, that is, the formation of a clear "whey" or serum within a reasonable time, but whether the quantity of acid necessary for this purpose is the optimum from the point of view of quality of the finished rubber, is another question.

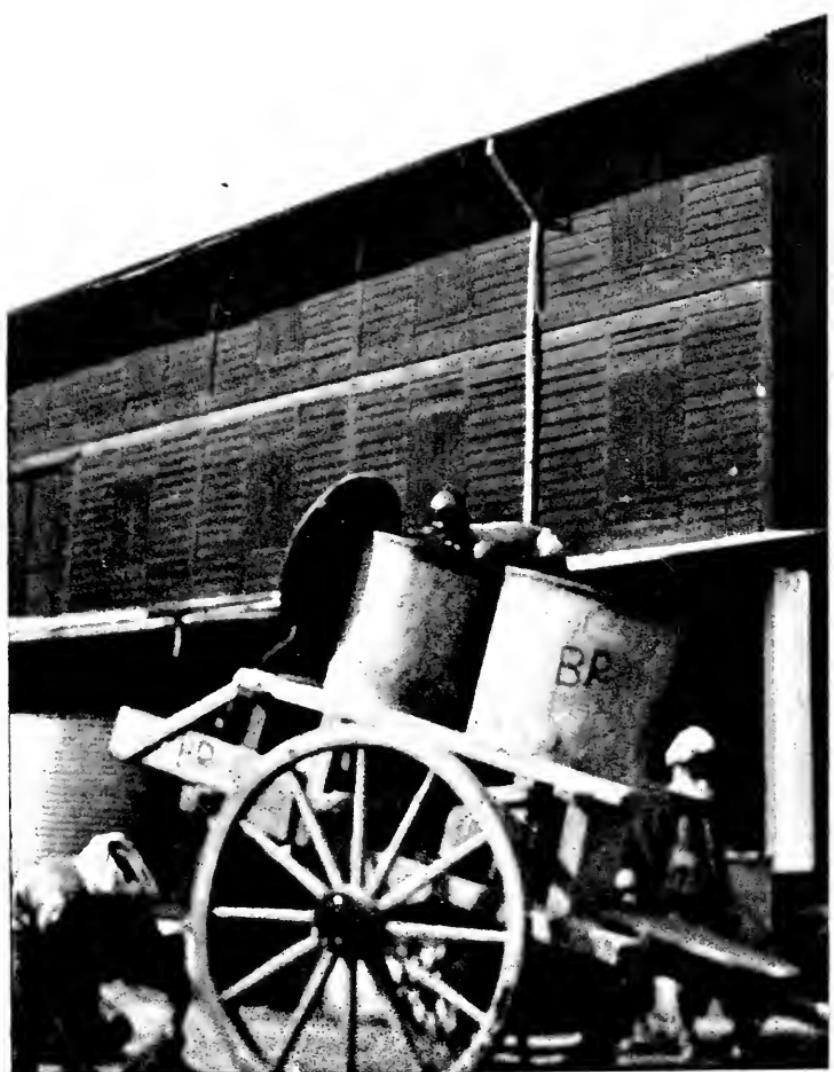
One of the first methods proposed for controlling the amount of acid required was that of employing an indicator, *e.g.*, of adding the reagent until litmus paper is turned faintly red by a drop of the latex. While this operation is one requiring some skill and judgment, it does not necessarily follow that it will give equally good results in all cases. It may quite well be, for instance, that the method will leave an equal excess of free acid in the case of a poor or watery latex, containing say 12 to 15 per cent. of rubber, and in a rich latex of double the rubber content. It is fairly obvious that the ratio  $\frac{\text{free acid}}{\text{rubber content}}$  is of importance in regard to the quality of the finished rubber, and irregular results are therefore likely to ensue if this test is used as the sole guide. Nevertheless, it is certainly preferable to employ some such method as this, than to adopt the haphazard policy of dosing the latex with an indiscriminate excess of acid such as I found in vogue on some estates in Malaya. Mr. Parkin<sup>1</sup> suggests that preliminary tests should be made on each lot of bulk latex by adding varying quantities of acid to equal volumes of diluted latex, boiling and noting the minimum of acid necessary to produce complete coagulation. According to him, the amount of acid required is the same in either heat or cold, and by heating coagulation is brought about very rapidly. I have never tried this method, but on purely theoretical grounds I very much doubt whether the cold "optimum" quantity of acid is the same as that required when heating, particularly if the quality of the rubber as well as the quantity is in consideration.

<sup>1</sup> *I.R.J., loc. cit.*

There is no doubt in my mind that in many cases far too much acetic acid is employed on the plantations, and that rotten, brittle rubber results. Rubber coagulated with an excess of acid dries rapidly compared with rubber prepared with a minimum, and this fact accounts for some of the evil doing in this direction. The reason for this more rapid drying is interesting. If a relatively small quantity of acid is added to the latex, the microscopic structure of the clot will tend to be that of a loose and rather wide mesh. As more acid is added this mesh tightens and becomes closer, and more and more liquid is squeezed from within the "honey comb" to the outside. If this tightening of the mesh proceeds beyond a certain point the material obviously loses elasticity. After a time, owing either to a specific action due to the excess of acid as such, or to traces remaining in the rubber, the material becomes brittle.

On the whole, I think that the best method of estimating the quantity of acid to be added would be that of adding varying quantities of acid to a number of samples of bulked latex and noting the minimum quantity which gives a good result and also the dry weight of rubber obtained in each case. This should be repeated say once a week, and gradually in this way the plantation manager would accumulate statistical material which would enable him to judge with comparative ease how any particular batch of latex (according to rubber content, time of year, plot from which derived) should be handled. If the acetic acid method is to stay, something of this kind will have to be done, otherwise the variability of quality in plantation rubber which is now a somewhat serious question is likely to continue. As an additional safeguard, the litmus test could be used constantly as a rough check.

I have made the above suggestions regarding the control of coagulation by the acetic acid method in the hope that they may be of some assistance to planters who are not in a position to avail themselves of direct scientific or technical advice, but it is necessary to point out that in view of the



ARRIVAL OF LATEX AT THE FACTORY  
(ON A SELANGOR ESTATE)



complex nature of the phenomena of coagulation and of the variability of conditions obtaining on the plantations, it is not to be expected that entirely satisfactory and consistent results will be obtained unless the problem is thoroughly investigated on practical and scientific lines. Fortunately the Rubber Planters Association of the Federated Malay States and kindred bodies in Ceylon and elsewhere are fully alive to this fact and have already taken steps with this end in view.

### *Other Methods of Coagulation*

*Experiments with the Para Method.*—The latex obtained under ordinary working conditions on the plantations contains appreciably less rubber, *i.e.* is more dilute, than the latex handled by the South American *seringueiro*. It is by no means easy to work dilute latex by the Para method, as the process becomes very tedious and the rubber is inclined to be—owing to the relatively lengthy heating of each individual film—sticky. It is more than probable that as the plantation trees increase in age, the latex will become richer in rubber generally, but as far as our present experience goes the stability of plantation latex, that is to say its capacity for remaining uncoagulated after collection, is inferior to that of the latex obtained from the Brazilian *Hevea*. If this should prove to be a permanent attribute, the use of water in the collecting cups will have to be continued, and the difficulty in regard to fluidity will remain.

Some interesting experiments on the Para method have been carried out by Dr. Ridley, the Director of the Singapore Botanical Gardens, with latex obtained from the old trees in that institution, and I had the privilege of seeing this work in operation. A sample of rubber thus cured was reported on by a firm of manufacturers as follows:<sup>1</sup>—

“With reference to your letter sending a small sample of Smoke Cured Para Rubber from the Singapore Botanical Gardens, prepared on exactly the same lines as hard fine

<sup>1</sup> *I.R.J.*, 1910, vol. xl. p. 685.

Para, we have tested this rubber and compared it with hard fine, with the following results:—

	Fine Hard Para.	Singapore Botanical Gardens Smoke Cured Para.
	Per cent.	Per cent.
Loss on washing .	18.00	13.00
Resin . . .	3.50	5.11
Organic matter .	1.50	2.03
Ash . . .	0.25	0.38

"In quality and general behaviour this rubber is extremely like fine hard Para in tensile strength and in power of recovery, but is slightly softer and requires a different vulcanizing heat.

"The elasticity and tensile strength for the period covered by the experiments show that at the proper vulcanizing heat it is as durable as Para. . . ."

Presumably these experiments were carried out with undiluted latex, a course which is, naturally, simple enough under expert supervision on an experiment station, but—at present, at any rate—impracticable on the plantation.

Notwithstanding the difficulties connected with the application of the Para system in the East, it is, in view of the importance of the question, rather surprising that so far no organized large scale experiments appear to have been carried out in this direction. It seems to me that the only practical method of deciding whether plantation rubber obtained by the Para method is superior to that made by the acetic acid process, and whether the Para method is commercially applicable under Eastern conditions, would be to have parallel experiments made in South America by the ordinary method of the country and by the acetic acid method, and conversely to have corresponding experiments made in Malaya. For the latter purpose a number of skilled *seringueiros* from Brazil should be induced to visit the Eastern plantations with a view to collecting and curing the latex in their own way.

Such experiments as I have suggested must, if they are to be of practical value, be conducted on large quantities of latex, and in various districts. At least half a ton of rubber should be made by each method both in South America and in Malaya, so that the products could be given a thorough trial in a rubber factory at home.

#### *“Smoking” by Mechanical Means*

Several machines have been devised for “smoking” latex in bulk, but so far as I am aware the difficulties connected with the adjustment of the temperature and volume of smoke to the flow of the latex have not yet been overcome to a degree sufficient to warrant a general departure from the ordinary method of coagulation.

#### *The “Da Costa” System*

The principle of this system is that of coagulation in bulk by the simultaneous injection of steam and smoke into the latex. I saw, on an Eastern plantation, a fair amount of crêpe produced by this system, and there was no doubt that, compared with the rubber produced by the acetic acid method in the same factory, the “Da Costa” rubber was stronger. I have found confirmation of this view by the examination of samples in the laboratory, and also of the general contention that rubber made in this way is more durable than acetic acid cured rubber—certainly than acetic rubber which has been overdosed with the acid,—but I have not yet been able to satisfy myself that the process is directly applicable to all *Hevea* latices. Heat alone will not coagulate fresh *Hevea* latex, and it seems reasonable to surmise, therefore, that where the process has given satisfactory results from the standpoint of complete coagulation, the original alkalinity of the latex has been sufficiently modified by exposure to cause the acid smoke combined with the mechanical action of the injected steam to bring about the desired results.

As the advantages of sterilization and smoking which the process involves are considerable, the difficulty regarding completeness of coagulation might well be overcome by using, when necessary, a very small quantity of acetic acid in conjunction with it.

#### *Formic Acid, Hydrofluoric Acid, etc.*

Formic acid, hydrofluoric acid, or preparations containing this substance or its salts and various other organic acids and salts, etc., have been recommended as coagulants for plantation work, and good results are stated to have been achieved by the use of some of them, more particularly of "Purub" (a fluorine preparation), but as I have no extensive personal experience of rubbers so prepared I can offer no opinion in regard to them.

#### ROLLING AND WASHING

The treatment to which the rubber coagulum is subjected has an important bearing on the quality and marketability of the rubber. The principles on which this treatment should be based are essentially simple, but as far as I can judge from my observations in Malaya, they are by no means thoroughly understood. One of two courses should be adopted—*(a) The rubber is merely sheeted by the action of the washing rolls.* Rubber rolled in this way retains an appreciable quantity of the non-rubber constituents of the latex, and must, therefore, in order to avoid mould or tackiness, be thoroughly antisepticized by smoking. *(b) The rubber is converted into crêpe and thoroughly washed during the process* with a view to removing the non-rubber latex constituents as far as possible. It is by no means certain as yet whether it is or is not desirable to remove the non-rubber latex constituents to the greatest possible extent, but it is quite certain that if the latter course is adopted, then, as is the case with Para rubber, the materialization of the potential capacity for mischief inherent in the small



A

TAPPING GOUGE (SEE PL. 61), COLLECTING CUP, STRAINER AND COAGULATING TIN ACTUALLY EMPLOYED ON A FIRST-CLASS SELANGOR ESTATE.



B

PART OF INTERIOR OF FACTORY (SUNGEI PULOH, FED. SELANGOR CO.)



quantities of soluble proteid, sugar, etc., contained in the latex, must be guarded against by smoking or some other form of antiseptization.

Para rubber contains all the latex constituents, is thoroughly smoked, film cured, and unsurpassed (as far as *Hevea* is concerned) for strength, elasticity, stability, and durability. Plantation sheet which contains a part of the latex constituents (other than rubber), obtained by a squeezing action (as opposed to the tearing or disintegrating action involved in making crêpe) and subsequently smoked, has, as far as manufacturing experience goes at the present time, given the most satisfactory results of the different plantation varieties. It has yet to be determined whether the superiority of Para and of "smoked sheet" is due to any material extent to the inclusion of the non-rubber latex constituents, and conversely to what extent the apparent inferiority of crêpe is due to the disintegrating action of the washing process. I am fairly satisfied that the smoking process not only antisepticizes the rubber and renders it stable, but that it also improves the strength and probably increases its capacity for resisting oxidation. Smoked crêpe pressed into block form yields, *ceteris paribus*, rubber excellent in strength and durability, and from the experience I have had in this direction it appears as though the disintegrating action of crêping may be largely compensated by subsequent pressure, *i.e.* by blocking, and to some extent also by the use of a "sheeter" (even speed smooth rolls) after crêping.

### *Washing Machines*

In the early days of the plantation industry, the soft rubber coagulum was put through a mangle or similar primitive appliance. The pressure thus applied has a two-fold effect—firstly, the serum is squeezed out to a considerable extent, and, secondly, the rubber is hardened.<sup>1</sup> At the present day the mangle has been replaced by washing

<sup>1</sup> In explanation of this phenomenon, see p. 126.

rolls, similar in general principles to those employed in the rubber factory (see Plate XVI.). The modern type of machine—which according to the setting of the rolls and the nature of the coagulum with which they are fed, may be used either for making sheet or crêpe—consists generally of two horizontal rolls running at differential speeds and provided with the usual fittings for the admission of water to the spray, for setting the rolls, with instantaneous disengaging gear, etc. *For making sheet* plain rolls are, in my opinion, the most satisfactory,<sup>1</sup> *for crêpe* plain, diamond cut, fluted or grooved rolls may be used, although I have a preference for somewhat finely diamond cut rolls working in series with a pair of plain rolls—the latter preferably running at even speed (see Plate XVII.).

With regard to *gearing*, a differential speed of 2:1 is not excessive for soft stuff, *i.e.* for making sheet or crêpe from a fresh coagulum, but in my opinion a lower ratio, say a difference of 20 to 30 per cent., is preferable for scrap or moderately hard material, particularly where a sheeter is not employed.

The modern tendency of making the rolls very wide, *i.e.* of increasing the ratio *diameter : length* as compared with ordinary factory rolls, is in the right direction in view of plantation requirements. Wide rolls are easy to adjust, reduce the chance of oil from the bearings getting on to the rubber to a minimum, and have advantages in regard to the production of a sheet or length of even size.

*Adjustment of Rolls.*—Ordinary washing rolls are adjusted by means of separate and independent set screws, and this method, if—as is essential for the production of a homogeneous sheet or length of crêpe and also to avoid tearing—the rolls are to be kept absolutely parallel, involves considerable skill and experience. Several machinery firms now make rolls provided with a simple single movement gear by means of which, after the preliminary adjustment after erection, a dead true adjustment is automatically maintained.

<sup>1</sup> Good “pressed” sheet can, however, be made with diamond cut rolls.



PLANCHON RUBBER WASHING MACHINE

(SEE FIG. 76)



Plate XVI. is an illustration of this type of machine as constructed by Messrs. David Bridge.

### *Sheet*

The washing or rather rolling of sheet is, as will have been already gathered, a very simple operation, and consists in passing the coagulum formed in the coagulating troughs once or twice through the rolls.

### *Crêpe*

On some plantations crêpe is the main product, and is made from strained latex coagulated in the factory. In other cases—particularly where smoked sheet is turned out—only “scrap” is converted into crêpe. “Scrap,” it will be remembered, are the lumps of coagulum which form in the cups, collecting pails, etc., prior to the arrival of the latex in the factory. Scrap must—as it is liable to contain a considerable quantity of mechanical dirt, etc.—be thoroughly cleansed, and this end is attained by a thorough washing on the rolls, the lumps being repeatedly passed through the machine until they have been reduced, by a gradual approximation of the rolls to one another, to an even crêpe band varying in length from say 12 to 40 feet, in width from say 8 to 14 inches, and in thickness from say one-sixteenth to three-sixteenths of an inch. Where crêpe is the main product and it is made from fresh coagulum, it can readily be turned out considerably thinner than one-sixteenth of an inch. Although thin crêpe dries rapidly and may be obtained very clean and light in colour, it is, on account of the relatively large surface exposed, very liable to oxidation, and I doubt whether, in the long run, this form will prove to be a profitable one, except, perhaps, for limited quantities for special purposes. It is not practicable to make thick crêpe (say three-sixteenths to five-sixteenths of an inch or more) in a single operation, mainly because it takes too long to dry. Thick or “blanket” crêpe should be obtained by running several superimposed layers of thin

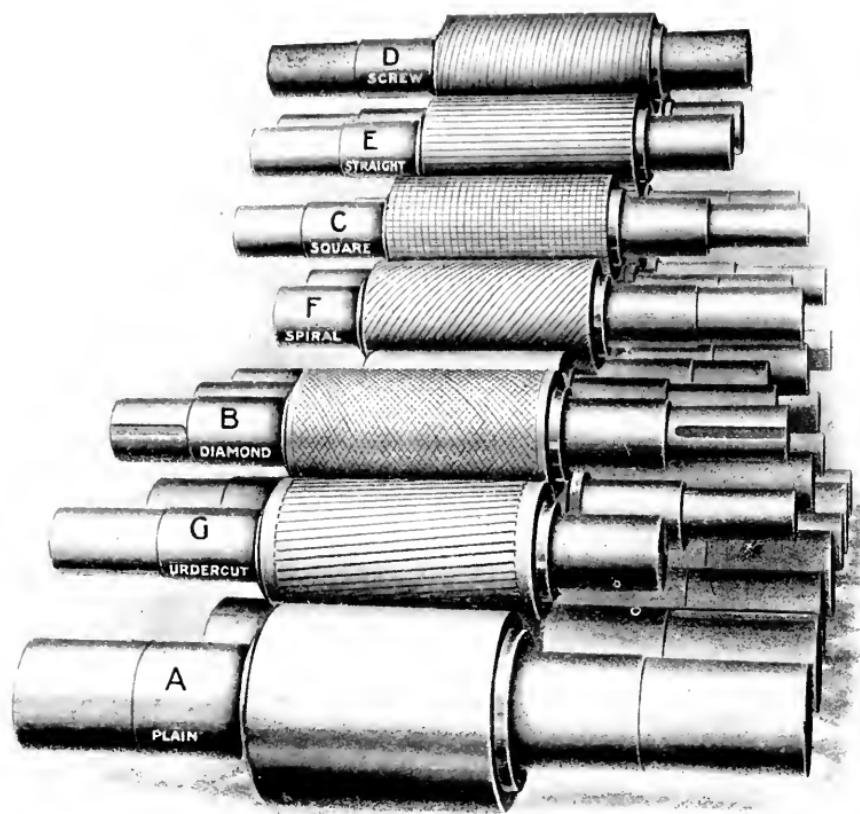
crêpe *after drying* through the rolls together, preferably while it is still warm from the vacuum drier or drying-house. For *block* rubber, see p. 84.

### Bark Scrap (*crêpe*)

The shavings of bark pared from the trees by the tapping process contain a considerable quantity of rubber, and this may be readily recovered by mechanical means in a more or less clean condition. The method employed is that of disintegrating the bark in such a manner (for instance, by differential friction in the presence of a stream of water) as to separate the bark from the rubber particles and to cause the latter to cohere. If a mass of bark shavings is passed repeatedly through a pair of differential rolls, preferably grooved or fluted, and a steady stream of water is maintained, the bark disintegrates and is gradually washed away, whereas the rubber particles tend to unite and finally emerge in the shape of a length of crêpe. As a preliminary, and with a view to shortening this somewhat tedious process,<sup>1</sup> the bark is occasionally first crushed by passing it in the *dry* state through a pair of rolls, sifting off as much dust as possible and then applying the process first mentioned. Bark scrap, of course, always contains more dirt or non-rubber than ordinary "scrap" (generally called No. 1 scrap) crêpe, and the latter in its turn is not so pure as the crêpe made direct from latex. The same graduation applies to the colour of the products.

In conclusion of the section on "Washing and Rolling," I may refer to the fact that if the rubber after the washing process proper be passed through a sheeter, *i.e.* a pair of even speed smooth rolls *set with accuracy*, the strength of the product is materially improved. If possible rolls should be run in series and set at fixed distances—for instance, a series of three rolls as follows: No. 1 diamond cut, differ-

<sup>1</sup> Modern machines (such as the Guiguet or Werner-Pfleiderer) specially designed for the purpose of treating bark and similar materials should prove much more satisfactory for treating bark scrap than are ordinary washing machines.



VARIOUS TYPES OF WASHING ROLLS

(SEE P. 76)



ential, set wide; No. 2, lightly cut, differential, but not to the same extent as No. 1, and set rather closer; No. 3, a sheeter, set close.

### DRYING AND CURING

It is now generally agreed that it is desirable to ship plantation rubber in a thoroughly dry condition. Should it be found practicable and advantageous to introduce a system of coagulation and curing similar to the Para method, this view may have to be modified, but the advantages of shipping rubber in a perfectly dry and clean condition are so important that any radical change in the direction indicated is not likely to come about, except as the result of very extensive further experiments. Rubber which is dry and clean is obviously more economical to ship than an article containing an appreciable quantity of extraneous matter; in other words, it is not desirable to pay carriage and freight on water and dirt. Dry, clean material shows, *cæteris paribus*, very little inclination to become mouldy or "tacky," and, what is perhaps the most important point of all, there is relatively little difficulty in judging the value of material of this description. It is, in fact, as nearly as possible an article of standard quality, whose merits or demerits are easily recognised and gauged. In the case of rubbers which are wet or dirty, the manufacturer is for all practical purposes the sole arbiter of price. He has to cover himself in regard to the "washing loss," to allow for the influence of varying degrees of "tackiness," and so on, and he, naturally enough, allows a pretty wide margin for his own protection. With rubbers of this description the seller is scarcely in a position to know whether he is getting full value for his goods, although when prices are high competition tends to narrow down the manufacturers' margin; but when a pure dry article is being dealt in, buyer and seller are practically on a level, and there is very little advantage on either side. It is true that rubbers which are

clean and dry may and do show considerable variation as regards colour, strength, durability and vulcanizing capacity, and that this variability may be greater than is the case with Para (which is shipped wet), but an examination of the causes which are responsible for the irregularity in quality of plantation rubber only serves to show that the trouble would be considerably accentuated if it were not shipped dry and clean.

### *Drying-Houses*

In erecting a drying-house the following essential considerations should be kept in mind :—

1. The material and construction should be so chosen that every part of the building may be easily and thoroughly cleaned by sluicing with a hose. With this end in view the walls, roof and floors should be smooth and all unnecessary angles avoided. The use of wood for the racks on which the sheets or crêpe are hung cannot well be avoided, but this material should not, if possible, enter into the construction of the building proper. Corrugated iron, cement and tiles are the most suitable material for general constructional purposes. The guiding principle is the same as that which obtains, say, in a malt house: there should be as little opportunity as possible for the lodgment of dirt and micro-organisms.

2. The ventilation of the building should be based on some rational scheme of steady air circulation, and not left to the haphazard opening and shutting of doors and windows. Doors, windows, ventilation ports and cowls should be so arranged that no direct sunlight or rain can enter. Draughts or a rapid rush of air through the building should be avoided. Ventilation fans are of doubtful value in small factories or where there is no expert supervision; in any case they should only be used as part of a general scheme of ventilation devised by a competent ventilation expert with a knowledge of rubber and its peculiarities.

3. Plenty of space should be allowed. It is better to

err on the side of excess of drying space than the reverse. A crowded drying-house does its work badly even with the best possible scheme of ventilation, besides which, particularly where the rubber is smoked, overheating is very liable to take place. There is no real difficulty in estimating drying space, provided that the estate manager has made up his mind what quantity and type of rubber he proposes to turn out. There is ample experience regarding the rate of drying of various types of rubber in different districts.

### *Hanging*

The simplest and probably best method of hanging crêpe in the drying-room consists in suspending it over cross battens about 4 inches apart, supported by upright and horizontal poles or narrow boards. The most economical disposition—which cannot, however, be used where an interior smoking arrangement is employed—is to have two tiers of battens, one above the other at a convenient height, so that the workman can, after mounting the stairway leading to the lower tier, easily pass the length of crêpe over the upper row of battens or drop them on to the lower row. A central gangway is not necessary or desirable, except in large buildings, as the workman has ready access to any part of either tier by walking over the lower row of battens. Sheets are generally much too short to be hung in the same way as crêpe, and are best suspended over racks, in a more or less horizontal position. A practical disposition is with three cross pieces, over the first and last and under the second. This method is, in my opinion, preferable to racks made of galvanized wire.

*Artificial heat for drying* should be if possible avoided. Rubber during the drying period is in an extremely sensitive condition, and it may be taken as a general rule that the lower the temperature at which it is practicable to dry, the better. If it were possible to dry rubber at a temperature not exceeding 70° F. "tackiness" would very rarely occur, and a great improvement in "nerve" would be

brought about. At present this is not practicable, but the temperature of a drying-house, even where vigorous smoking is in force, should and can be kept below 100° F. It is necessary to be emphatic on this point, as the proposal to dry with hot air at high temperatures has been repeatedly made, and appears to have borne fruit, for while in Malaya I saw a drying-house in course of erection in which steam-pipes were being put in with a view to drying off at 140° F.! If this policy is carried into effect, I should not be surprised to see the rubber from this particular estate arrive home in the shape of treacle.

#### *Drying with Cool Dry Air*

The ideal method of drying would be in air-tight chambers through which a steady current of *dry* air at about 70° F. was passed. There are many practical difficulties in the way of such a method, the first of which is the drying of the intensely moist air of the rubber districts. Sulphuric acid, calcium chloride and other chemical driers have been proposed, but are quite obviously out of the question from a technical point of view. It seems strange to me that the only practicable technical method of drying air on a large scale which might be suitable for rubber drying-houses, namely, that of *cooling the air* to the condensation point of the bulk of the contained moisture, has, as far as I am aware, never been suggested. Such plants are made for the purpose of producing liquid air, of ice-making, etc., and should be, without very great modification, adaptable for the purpose indicated. An advantage of this method would be that both the desired conditions, namely, those of cooling and also drying the air, would be attained in one operation. Relatively dry air at say 70° to 75° would obviously reduce the drying time enormously, not to speak of the improvement in the rubber which would undoubtedly result. At present crêpe of medium thickness will take say ten to twelve days to dry. With dry air at the temperature suggested, the same result would probably

be achieved in much less than half the time. I admit that—putting aside the probable improvement in the quality of the rubber, which, at present, one is scarcely in a position to translate into commercial terms—it is questionable whether a saving of time alone in drying is worth any considerable capital expenditure in the majority of cases, but I may say that I have known instances where time was a highly important factor, and will leave it to the judgment of those most interested to consider whether a saving of 50 to 60 per cent. of drying time at some, but by no means prohibitory, capital expenditure, is of any financial moment.

### *Smoking*

Two main methods of "smoking" may be considered—

- (a) The exterior furnace; (b) the interior smoke box or brazier.

(a) *Exterior furnace*.—The main advantages of having the smoke-producing apparatus outside the rubber house is that much space is saved and building expense reduced by perhaps 30 to 50 per cent. I am aware that in many cases interior smoke boxes, let into the soil over which the building is erected, are employed, but this method seems to me crude and undesirable in many respects, and I am, therefore, not taking it into consideration. The disadvantages of the exterior furnace are that it is difficult to regulate the feeding and draught so that the main object, namely, that of obtaining a liberal supply of smoke and at the same time prevent over-heating of the drying-house, may be attained.

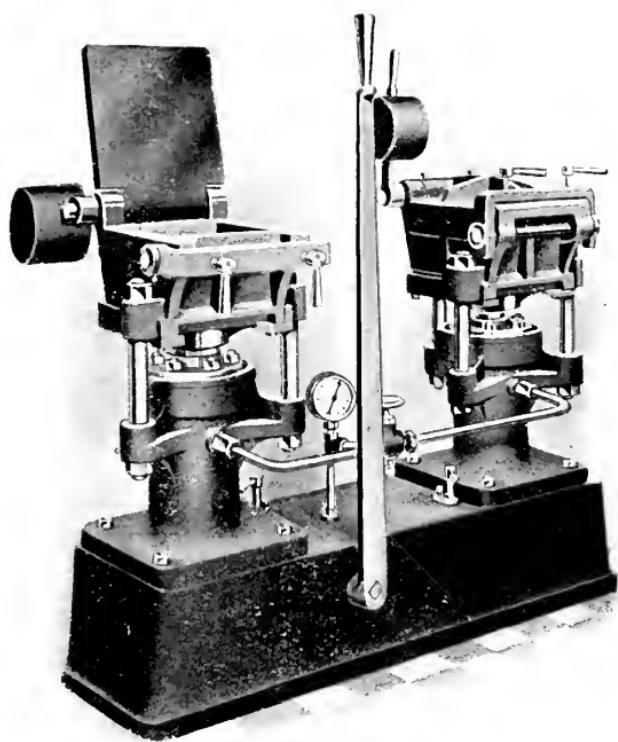
(b) *Interior smoke box or brazier*.—The simplest method consists in having an open brazier standing on the bare earth on the ground floor of the building. Above this there should be a baffle plate for the purpose of stopping sparks and distributing the smoke. If the walls of the lower part of the building are built at an angle, *i.e.* slope inwards from the line of the upper floor to the earth, much space is saved and a good distribution of smoke is achieved. The floor of the upper part of the building is made on much the same

lines as a Scotch malt kiln, of tough wire-netting or of perforated tiles. The roof should be hung loosely with canvas so that condensing tar may not drop on to the rubber.

*Material for Smoking.*—Practically any hard wood, cocoa-nut husk, air-dry peat, or similar material, may be used for smoking. The idea that any substance—such as the much advertised *urucuri* nut of Brazil<sup>1</sup>—possesses particular virtues in this direction, is, in my opinion, pure nonsense. I have reproduced the exact Para odour (and effect) with air-dried Scotch peat, with an earthy peat cut from swampy ground in Borneo, and with various woods and cocoa-nut husks from Malaya, Borneo, etc.

*Effect of "Smoking."*—Smoke not only acts as an excellent antiseptic and preservative, but, according to my experience, improves—for some reason yet to be explained—the strength of the rubber. I am surprised that smoking is not resorted to more generally than is the case. Thus mildew in sheets, which is of quite common occurrence and causes much grief to many estate managers in the East, is absolutely unknown where smoking is resorted to. Smoking, it is true, affects the colour somewhat, but the prices which are now being fetched by smoked sheet indicate that this is a matter of small moment. In the future very pale rubber will no doubt, as now, be in demand for certain purposes, but such demand is always likely to be a limited one, and I think that where an advantage in regard to colour is got at the cost of strength and durability, more is lost than is gained. Personally I should like to see the bulk of the plantation crêpe smoked as well as the sheet. A form of plantation rubber of which very little has yet been seen is *smoked block* made from smoked crêpe. Blocked rubber, *i.e.* rubber in crêpe form, which has been compressed in a blocking machine (see Plate XVIII.), is undoubtedly stronger and more durable—provided that it has been blocked at a

<sup>1</sup> “Up-river” fine Para, *i.e.* the “hard” variety, is mostly smoked with hard wood only.



BRIDGE'S HYDRAULIC BLOCKING PRESS FOR CRUDE RUBBER  
(SEE P. 84)



relatively low temperature—than ordinary sheet or crêpe. As far as quality is concerned, smoked block—I am not taking into consideration the possible application of the Para method—should be the ideal form, but the drawback to block is that manufacturers object to it on account of the time and labour requisite for cutting it up. Planters should, however, understand that this objection cannot reasonably apply to thin block (say 1 to  $1\frac{1}{2}$  inch thick), that is to say, to material which will be taken by the washing or mixing machine without previous cutting up. On the other hand, the making of thin block is rather a nuisance, and I am by no means certain that the best plan might not be to make large blocks and then to cut them with a suitable machine into sections of about 1 inch, *on the plantation*. No doubt there will always be a good demand for crêpe, but I am willing to prophesy that “the manufacturer will not have block” will gradually die away when he comes to appreciate the advantages of the smoked slab or thin block.

#### *Vacuum Drying*

By drying rubber by the vacuum process, that is to say in a closed vessel, heated by steam and from which the air and moisture are exhausted by means of a vacuum pump, it can be obtained in a translucent and commercially dry condition, roughly speaking, in as many hours as it takes days by the ordinary air-drying method. Vacuum drying is particularly applicable to thin to medium crêpe and sheet. While a vacuum dryer is an expensive piece of apparatus, the cost and upkeep of buildings and the saving of space as well as of time must be set against its prime cost and working expenses. Nevertheless, the vacuum dryer has made no great headway in plantation work, mainly because, if not carefully handled, it is liable to yield sticky rubber. Some rubbers, however carefully handled, do certainly not give good results in the vacuum dryer. The effect of a vacuum—even at moderate temperatures such as  $90^{\circ}$  to  $100^{\circ}$  F.—

on a rubber which is naturally inclined towards tackiness, appears to be that of promoting its physical dia-aggregation (or depolymerization). It has, in fact, the reverse effect of pressure. In the case of plantation *Hevea* obtained from reasonably mature trees and prepared on proper lines, this should not be the case, and if certain precautions are observed, the vacuum dryer should (and, as a matter of fact, does) give good results. In working the vacuum dryer there should be no sudden rise either of temperature or of vacuum. What the temperature maximum for safe working is cannot be stated definitely, as it varies appreciably for different rubbers, but at temperatures not exceeding 100° to 105° F. very good results may be obtained even with softish rubbers. On the other hand, it must be remembered that low temperatures in vacuum drying mean a lengthening of the drying period, and consequently a partial loss of the main advantage inherent in the system. A disadvantage of vacuum drying is that the rubber cannot be "smoked" simultaneously with the drying operation. The vacuum dryer, however, much facilitates the manufacture of "block," the warm rubber, as it comes from the machine, being in a condition peculiarly suitable for this purpose.

#### COLOUR OF PLANTATION RUBBER

While strength and durability are the most important qualities, the colour of rubber is by no means a negligible factor. For certain classes of goods a very light colour is desirable, but this class of goods is limited in extent. There has been a tendency on the part of plantation companies to over-rate the importance of colour; but a reaction is now setting in, and the fact that evenness of colour is more important than the actual shade is beginning to be appreciated. Plantation *Hevea* (and for the matter of that, other rubbers as well) may be obtained in a practically colourless condition if steps are taken to remove the substances which are responsible for its coloration. In the case of *Hevea*

latex this substance appears to be a simple enzyme, and its removal or destruction may be readily brought about. Mr. Kelway Bamber<sup>1</sup> has shown that if fresh *Hevea* coagulum is heated to a temperature of about 180° F. by passing it through hot water, the rubber subsequently undergoes very little change in colour, and in thin sheets or crêpe remains almost white. Very pale rubber—I have seen practically white specimens prepared—can, however, be obtained without this heating process, merely by paying very great attention to the cleanliness of all the utensils and apparatus employed, and by very carefully washing the rubber after coagulation. But, notwithstanding these facts, it does not appear to be possible to produce rubber equally light in colour in every district. There is considerable variation in regard to the colour of the latex itself, and this in its turn is mainly due to differences in the soil. I was informed on very excellent authority that the latex in a certain district in the north of the Federated Malay States emerges from the tree almost black, but it is necessary to add that I have no personal experience of such an extreme case as this.

## FUTURE OF THE PLANTATION INDUSTRY

### ADVANTAGES AND DISADVANTAGES

The future of the plantation industry may, broadly speaking, be said to be definitely bound up with the three following factors: (a) The quality of the rubber produced; (b) the cost of production; and (c) the competition from other sources. In addition there is, of course, the somewhat uncertain factor of the demand, which necessarily dominates the situation as a whole.

Before considering the question of the future of the plantation industry, it may be well to set out a few further facts regarding its present extent. I have already referred to the approximate planted acreages, also to the total areas

<sup>1</sup> *Lectures*, 73.

alienated for rubber in various Eastern districts, but it may be of interest to supplement this information by some figures referring to the capital invested.

#### CAPITAL INVESTED<sup>1</sup>

Invested 1906-1909	.	.	.	.	.	.	£24,290,260
,, 1910	.	.	.	.	.	.	38,841,500
Total 1906-1910	.	.	.	.	.	.	£63,131,760

The amount invested in 1908 was £2,014,500, in 1909 £13,671,000.

These figures are, of course, based on publicly issued capital; in addition there must be a very considerable sum representing private capital. It is probable that the total investments in the plantation industry are not far short of 70 millions sterling. Some idea of the distribution of this capital may be gleaned from the following figures:—

#### AMOUNTS INVESTED IN VARIOUS COUNTRIES IN 1910

Malaya	.	.	.	.	.	.	.	£8,337,000
Java	.	.	.	.	.	.	.	5,970,000
Africa	.	.	.	.	.	.	.	6,064,500
Borneo	.	.	.	.	.	.	.	3,680,000
Ceylon	.	.	.	.	.	.	.	3,920,000
Sumatra	.	.	.	.	.	.	.	2,240,000
Brazil	.	.	.	.	.	.	.	2,350,000
Mexico	.	.	.	.	.	.	.	1,775,000

#### (a) Quality of Planted Rubber

Various points connected with the quality of plantation rubber as compared with Para and other rubbers have already been discussed. As far as the present-day experience of manufacturers goes, the consensus of opinion appears to be that the best plantation rubber can be used for practically all purposes for which Para is employed, but that for certain special purposes, for instance, for the manufacture of elastic thread or sheet, it can either not be

<sup>1</sup> Cf. *I.R.J.*, 1911, vol. xli. p. 102, and *G.Z.*, 1911, vol. xxv. p. 496.

employed or gives results inferior to Para. Cut sheet is an article the commercial importance of which is rapidly decreasing. Elastic thread, while it was used to a very large extent formerly for spring-side boots, has also lost some of its importance since these have gone out of fashion, but it is still largely employed for such articles as braces, surgical goods, etc. I feel reasonably certain that when the supply of mature plantation rubber increases, and when the variability of the plantation product is got over by more rational methods of coagulation and curing, that it will be possible to use it for every purpose for which Para is now employed. The strength and other attributes of rubber are so largely capable of modification by proper treatment of the latex, that it is rash to assume that the quality of rubber derived from a particular species in any one part of the world will permanently remain appreciably different from that obtained in another part, if, as is the case in comparing the Eastern plantations with Brazil, soil and climate appear equally suitable to this species in both cases.

(b) *Cost of Production*

There are two main factors to be considered in this connexion—(a) Cost of bringing into bearing; (b) upkeep and manufacture. The cost of bringing into bearing varies from £18 to £20 per acre upwards, and if the average be taken at £40 per acre a conservative basis of calculation is assured. At 5 per cent. this corresponds to a fixed charge of £2 per annum, or assuming that 240 lb. per acre are produced, to 2d. per lb. of rubber. With regard to upkeep and manufacture the following figures are based on the actual working expenses of a Malay estate which was producing about 100 tons of rubber at 200 lb. to the acre at the time when the calculation was made, and which was estimated when mature to produce 400 lb. to the acre.<sup>1</sup>

<sup>1</sup> H. K. Rutherford, *I.R.J.*, Quarter-Century Number, 1909, p. 60.

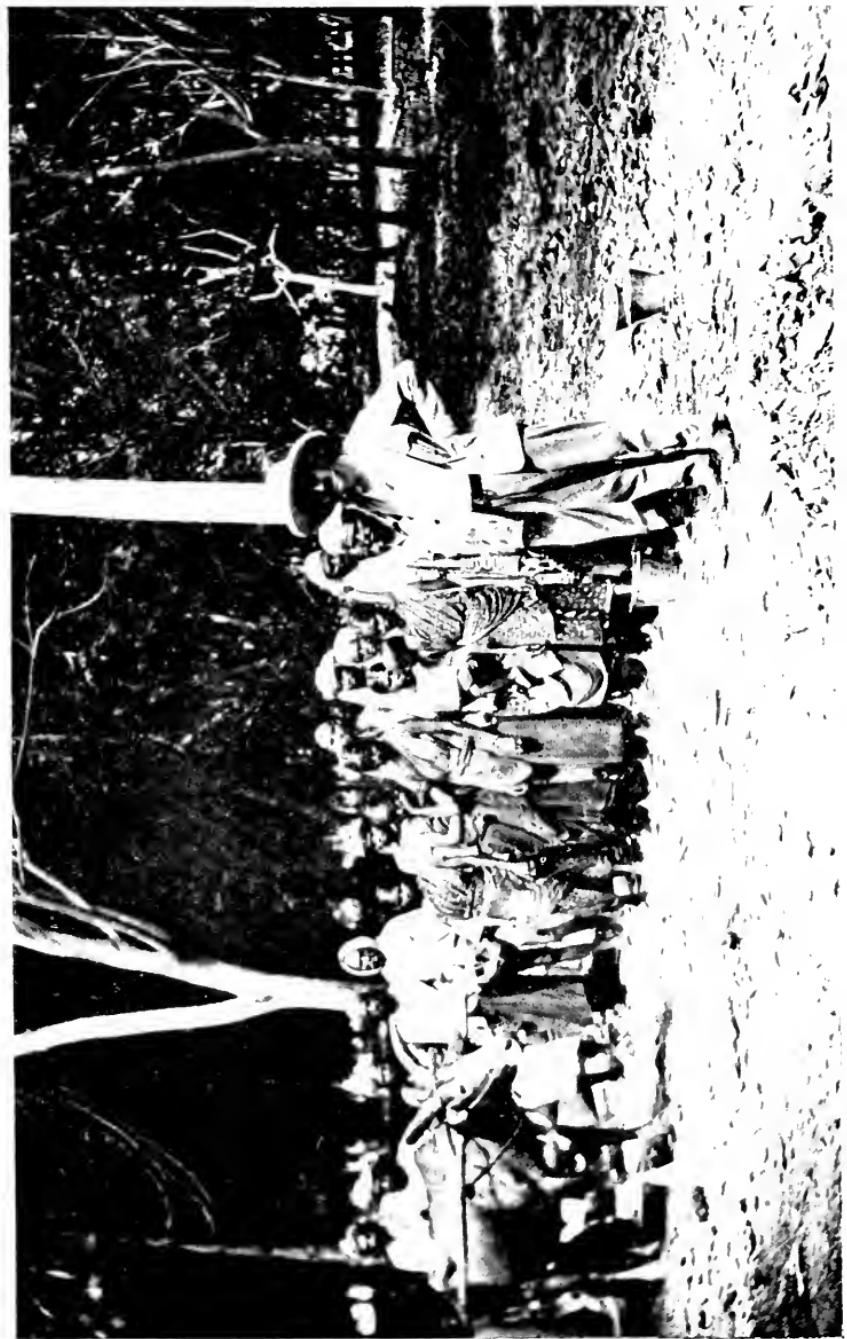
## RUBBER

	Per lb. of Rubber produced.
<i>General Charges—</i>	
Salaries, allowances, quit rent, hospital, contingencies . . . . .	2.31d.
<i>Cultivation Charges—</i>	
Weeding, roads, drains, supplying, pests and diseases . . . . .	1.85d.
<i>Upkeep of Buildings</i> . . . . .	
<i>Rubber Manufacture—</i>	
Tapping and scrapping . . . . .	3.93d.
Curing . . . . .	0.43d.
Packing . . . . .	0.33d.
Marking, utensils, transport, etc. . . . .	0.47d.
Duty . . . . .	1.19d.
Manufacture total . . . . .	6.35d.
<i>Total Working Charges</i> . . . . .	10.74d.
	per lb. of rubber.
<i>Total Charges—</i>	
Fixed : : : : .	2.00d. <sup>1</sup>
Working : : : : .	10.74d. (details above <sup>2</sup> )
Total . . . . .	12.74d.

To place the rubber on the European market a further 3d. to 3½d. (freight, brokerage, insurance, etc.) must be added, making a total of about 1s. 4d. per lb. There is very little doubt that the estate in question would when producing at its full capacity turn out rubber which, other things remaining equal, could be placed on the European market at 10d. to 1s., and there is no doubt that particularly well placed estates can produce and sell rubber (landed in Europe) at a profit in the neighbourhood of 1s. per lb. Before considering the questions which may affect cost of production in the future, it may be of interest to refer to the basis on which such production has been very generally estimated, and as a corollary the valuation of rubber estates on this basis. A reasonable method, and one which has been very largely employed in valuations of this description, is that comprised in the so-called Malcolm-Cumming scale, devised by the well-known plantation expert of that name.

<sup>1</sup> Estimated by the writer.

<sup>2</sup> According to Rutherford.



TAMIL LABOUR  
(ON ERUVI RAJAH ESTATE, SELANGOR)



Mr. Cumming proceeds on the basis of a five year purchase calculated on the net profits derived from the rubber sales. He estimates that trees in their 5th year will yield 100 lb. of rubber, in the 6th year 200 lb., trees at 7 years and subsequently 300 lb. per acre. Using this scale in 1910, he allowed a profit of 5s. per lb. in the 1st year, 4s. per lb. in the 2nd, and so on down to 1s. per lb. in the 5th year. Worked out on this basis the value of an acre at different ages would be as follows:—

1 acre newly-planted rubber	.	.	.	.	.	.	£5
„ 1 year old	.	.	.	.	.	.	20
„ 2 „	.	.	.	.	.	.	50
„ 3 „	.	.	.	.	.	.	95
„ 4 „	.	.	.	.	.	.	150

During the year 1910 the profits of a number of companies largely exceeded those which are estimated by the Malcolm-Cumming scale, but whether two years hence plantation companies will be earning a profit of 3s. per lb. and three years hence 2s. per lb. must be regarded as somewhat doubtful.

### *Question of Labour*

In my opinion the most important point to be considered in connexion with the future cost of production is that of labour. At the present time the bulk of plantation labour in Malaya is drawn from Southern India and consists of Tamils. A small proportion consists of Javanese, Chinese, and Malays. It is a remarkable fact, which, by the way, I was able to confirm by personal observation and inquiries, that the Malays—the natural inhabitants of the country—have a rooted objection to working on plantations, or in fact to any kind of work involving routine and the sinking of individuality. The Malay will readily cut paths through apparently impenetrable jungle and fetch out wild rubber and other jungle products; as long as he is practically his own master he will work intelligently, skilfully, and sufficiently hard—if it is made worth his while. This character-

istic of the Malay is likely to be felt somewhat acutely in the future, for there are already signs that the Governments respectively of India and Java will not be able indefinitely to permit the continued emigration of labour from these countries. It may be necessary ultimately to have recourse on a large scale to Chinese labour. The ordinary Chinese coolie is not particularly well suited for individual work, such as tapping, but he is excellent for mass work, such as clearing and weeding. In some respects the Chinaman is similar to the Malay in regard to individual work. The better class Chinese coolie will do excellent individual work if he is his own master, but is not particularly anxious to do work requiring some individual skill for a low rate of pay. There is a wide gulf between the Chinese skilled labourer and the ordinary coolie, this difference being a great deal more marked than is the case with similar classes of labour in the Occident. Under the supervision of a skilled *mandor*, as the Chinese overseers are called, the ordinary Chinese coolie may be trained to do practically any kind of work, and there is no doubt that if it is necessary to employ Chinese coolies on a large scale, they will be found, with training, to be capable of everything that is necessary. It is not yet possible to say what the effect of a large demand for Chinese labour will be, but it must be borne in mind that the Chinese labour recruiting agents are past-masters in the art of trade unionism and in reaping the benefits of the opportunities which offer themselves. There are also signs that China is requiring more and more labour for her own purposes. I am inclined to think, therefore, that the question of labour is likely to play a somewhat important part in the future in regard to the cost of production. Should the cost of production be appreciably raised as the ultimate result of the labour difficulty, this would perhaps not be an unmixed evil, for it would in its turn tend to counteract over-production by eliminating the competition of the less favoured districts.

*Diseases and Pests*

Another factor which must be considered in connexion with the cost of production in the future is that of epidemics which may be produced by diseases and pests. Experience in connexion with other tropical products has shown that if a large area is planted with a single species the danger from this source is considerable. Planted *Hevea* is liable to a number of diseases affecting the roots and body of the tree, but so far nothing has arisen to suggest that with ordinary care these may not be kept down. Nothing in the nature of an epidemic or widespread disease has yet occurred, and, on the whole, I think it may be fairly said that planted rubber compares favourably in this regard with other planted tropical growths, particularly as practical experience of rubber-planting now extends over a considerable number of years. The plantation interests and Government departments concerned appear to be fully alive to the importance of this question, and although one cannot speak with absolute certainty, it appears probable, in view of the constant and scientific supervision which is now being exercised, that the question of epidemics may be regarded as an important but not menacing factor from the point of view of the continued success of the plantation industry. Of the various diseases and pests which have so far shown themselves, only two need be referred to, namely, the fungus growth *Fomes semitostus* (white thread disease), and *Termes gestroi* (white ants). According to Mr. Alma Baker,<sup>1</sup> the signs of *white thread disease*, also known as "root" disease, are as follow: (1) The tree presents a dried-up appearance caused by the cobweb threads round the root cutting off supplies; (2) the tree holds loosely in the ground (this can be detected by shaking); (3) the tree possesses a sunken-in appearance on one side of the stem, low down on the side attacked. Various remedies have been proposed for this disease, based on the general principles of antiseptic treat-

<sup>1</sup> *I.R.J.*, 1910, vol. xl. p. 306d.

ment and isolation, and it appears that where the general conditions of drainage and weeding are satisfactory the disease is little liable to occur.<sup>1</sup>

*White Ants.*—The white ant is a perennial source of mischief in the East, and its destructive capacities are well known. It does not appear to have a special predilection for *Hevea*, and, according to Knocker,<sup>2</sup> they will not attack *Hevea* if there is any other source of plant food at its disposal. The most suitable method of dealing with white ants which have attacked a tree appears to be that of injecting vapours of carbon bisulphide into their nests. Sulphur and arsenic fumes are also used for this purpose.<sup>1</sup>

*Degeneration.*—It has been suggested that plantation trees may gradually degenerate, particularly those which have been planted from weak seed, and while it is possible that this may occur, it does not, according to the experience gained so far, appear to be at all probable.

### (c) *Competition from other Sources*

There appears to be a prevalent opinion to the effect that ultimately either wild or plantation rubber must "go to the wall," and that it is much more likely to be the former than the latter. While there is much to be said for this view, it fails to carry conviction to my own mind. There are good, bad, and indifferent plantations, just as there are good, bad, and indifferent wild rubber areas. The first rubber to go will undoubtedly be that which is not prepared in a cleanly fashion. "Africans" as we know them now will be a thing of the past, and that very shortly. It does not, however, follow that the rubber forests of Africa will no longer furnish their quota to the world's supply. On the contrary, it seems to me that the system of rationally working forest areas on semi-plantation lines—as is the case, for

<sup>1</sup> For details regarding the disease, method of treatment, etc., see Alma Baker, *loc. cit.*, and W. J. Gallaher, "Bulletins Nos. 2 and 3" (*F.M.S. Government Reports*).

<sup>2</sup> *Rubber-Planting in the Malay States* (De-la-More Press, Lond.), pp. 42 *et seq.*

instance, in the Mabira Forest—is likely to be extended. It is true that it involves the cost of cutting roads and that the cost of collection is relatively high, but numerous areas on which the trees occur in fair numbers, and in which there is a sufficiency of intelligent labour, are to be found. While the plantation possesses as its main asset the advantage that it is possible to obtain, under skilled white superintendence, on a minimum area a maximum of (high-class) rubber, the cost of bringing into bearing is relatively high. The wild tree costs nothing for production or upkeep. Personally I believe that for a number of years to come there will be no question of any vital struggle between "wild" and cultivated rubber. It has recently been suggested<sup>1</sup> that there may be something in the quality of the Amazon rubber which will make the continuation of the supply a necessity for the manufacturers; but it will have been gathered from what I said on p. 88 that I am not in agreement with this view. The whole crux of the situation lies in the labour question. If Sandmann's<sup>2</sup> views are correct, namely, that by reorganizing the food supplies on the Amazon, remitting the present outrageous taxation and opening up the foot-hill districts, the Brazilians will ultimately be able to produce "fine hard" at the same price as the plantations are turning out their product, then, indeed, other sources of production will have to look to their laurels, but meanwhile it may be pointed out that, notwithstanding the extraordinary demand in 1910 (the "boom" year) the Para supplies were actually smaller than 1909. It must not, however, be forgotten that labour difficulties may and will most probably arise on the plantations also, and that the cost of production may thus rise to say 2s. a lb. all round. This, however, would not necessarily be an evil, as it would prevent the indiscriminate further planting of a product, which, as a writer in *The Times* (*cf. loc. cit.*) points out, is likely to continue as long as there is a chance of the material being sold at a

<sup>1</sup> Cf. *The Times Commercial and Financial Supplement*, January 6, 1911.

<sup>2</sup> Cf. p. 28.

profit. There is no monopoly in planting. While general economic principles point to the practical certainty of an eventual over-production, it appears to me that this is not likely to come for a considerable number of years.

### *Increased Demand*

The statistics on pp. 12-19 warrant the inference that an increase of at least 10 per cent. in the demand is probable. If we take the consumption for 1911 as being 85,000 tons, and allow for an increase on the lines indicated, we get for 1916 a normal consumption of nearly 137,000 tons, as against a possible production (cf. p. 15) of 145,000 to 160,000 tons. About 1915 to 1916, therefore, the production *may* begin to exceed the normal consumption. Normal consumption implies normal prices, say 4s. to 5s. per lb. Directly production overtakes normal consumption, prices will drop, and this, undoubtedly, will lead to an increased use of rubber, that is, to an increased normal consumption. From these assumptions—for, after all, there can be no absolute certainty in this matter—I come to the conclusion that up to 1916 there will be, for all practical purposes, no vital competition between different classes of high grade rubbers. After that, I am equally certain, favourably situated, well managed and not over-capitalized plantation estates will still have no difficulty in holding their own, whatever “wild-rubber” developments may take place on the Amazon or elsewhere. If the Amazon can reorganize on the lines indicated by Sandmann, it is possible that there will be a serious struggle between South America and the plantations *as a whole*—I exclude the best class—but at the present there is nothing to indicate that this is likely to be the case. The whole question may be summed up as follows: good plantation and good forest undertakings will survive, bad plantations and unsound “wild” undertakings will go to the wall; but it looks as though even the weaklings will have a number of years of grace.

## CHAPTER VI

### THE PREPARATION OF RUBBERS OTHER THAN *HEVEA* ON THE PLANTATION SYSTEM

THE remarkable development of the Eastern plantations has naturally led to many attempts to apply the basic principles of that system to other varieties in different parts of the world. As far as the Eastern plantations, however, are concerned, it must be borne in mind that the almost exclusive planting of *Hevea* is not the result of any haphazard policy, but that it has been the final step in a series of extensive practical experiments carried out with a view to ascertaining which is the most suitable tree for planting in these regions.

The general result of experiments in various parts of the world has confirmed the fact that *Hevea* is under most conditions the best and hardiest producer. Its growth is rapid, the production period is reached at a relatively early stage, the rubber yield is larger than that of any other practicable tree, and its resistance to diseases and pests has so far been satisfactory. Moreover, the quality of *Hevea* rubber is of the highest grade, and the experience of a practical nature accumulated in connexion with *Hevea* as a plantation tree immeasurably transcends that obtained with any other species.

Nevertheless, under certain conditions and for special reasons, other species have been planted, partly experimentally, partly because they have seemed to be most suited to the local conditions. Thus *Manihot Glaziovii* (Ceara rubber) and *Jequie Manihot* will certainly thrive in soil which is too

poor for *Hevea*, and the *Manihots* develop reasonably well in regions in which the rainfall is insufficient for the latter. In certain countries the species indigenous to and characteristic of the region has been planted on a considerable scale, and with, according to most accounts, a fair amount of success, for instance, *Castilloa elastica* in Mexico, *Manihot* (*Glaziovii* and *dichotoma*) in parts of South and Central America and Africa, and *Funtumia elastica* in Uganda, the west coast of Africa, etc. On the other hand, the common natural (forest) rubber tree of the East, namely, *Ficus elastica* (Rambong rubber), has, broadly speaking, not proved a success from a planting point of view.

### *CASTILLOA ELASTICA*

According to Olsson-Seffer, Russan, and others, this tree is certainly the most suitable for Mexico, and it is stated that more than 100,000 acres<sup>1</sup> are planted with this species in that country. According to Russan<sup>2</sup> the yield of rubber that may be expected from *Castilloa* in the State of Soconusco is as follows :—

Age (years)	6	7	8	9	10	11	12
Yield (lb.)	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{3}{4}$	2

This, of course, is far lower than the corresponding figures for *Hevea* (see p. 63).

The latex from young trees, or from trees grown under unfavourable conditions, is very resinous. With age the resin tends to disappear. This is a characteristic of *Castilloa*. According to Olsson-Seffer,<sup>1</sup> *Castilloa* is preferable to *Hevea* in Mexico, for the reason that while *Hevea* grows well in Mexico and gives good yields, there are certain local conditions against it. In order to obtain a full yield from the *Hevea*, it is necessary to tap as many as 150 to 160 times

<sup>1</sup> Olsson-Seffer, *The American Review of Tropical Agriculture*, March-April, 1910.

<sup>2</sup> I.R.J., Quarter-Century Number, p. 85.



A  
*FUNTUMIA ELASTICA*  
(FLOWER AND FRUIT)



B  
*FUNT. ELAST.*  
(FOREST SEEDLINGS, 3-4 MONTHS OLD - MAITRA FOREST)



C  
*A FINE HEADED FUNTUMIA ELASTICA*  
(IN GOMA, MAITRA FOREST)



D  
*LANDOLPHIA FL.*  
(FLOWER AND FRUIT)



per annum to produce, say, 2 to 3 lb. of rubber. On the other hand, 1 lb. of rubber can be obtained from a 12 year old *Castilloa* tree by means of four or five tappings per annum. The question of labour, therefore, appears to be a decisive item, and according to Seffer labour is so expensive in Mexico that it costs far more to produce a pound of *Hevea* than a pound of *Castilloa*. According to Seffer *Castilloa* may be planted as close as 400 trees to the acre for mature trees, and he states that, taking this into consideration, the yield is better for *Castilloa* per acre than for *Hevea*. Mr. J. B. Carruthers, late Government Botanist and Assistant Director of Agriculture for Trinidad and Tobago,<sup>1</sup> in a report published shortly before his death, was not able to come to any decisive conclusion regarding the future of *Castilloa* in the West Indies, although the tree thrives very well in these parts. According to Carruthers there were at least 600,000 *Castilloa* trees in Trinidad. But from the results obtained with these and from the information obtained elsewhere he came to the conclusion that the plant neither in the West Indies nor in Mexico gives anything like as large a yield as does *Hevea* in Malaya or in Ceylon. H. J. Ludewig<sup>2</sup> states that the total export of *Castilloa* from Mexico amounted to 911,200 lb. in 1908-9, and that, taking the yield of a 10-year old plant as 150 grms. (5.3 oz.), and 200 trees to the acre, a total yield of about 6 million pounds may be expected in 1915. According to Ludewig the expectations with respect to the *Castilloa* are far from being fulfilled. In Palenque there are well-developed 14-year old trees yielding no latex, while on the most promising plantation—one of 1235 acres with 350,000 6 to 8 year old trees—the yield is no more than 3.7 oz. per tree. There appears therefore to be a very wide variation in the yield that may be expected from *Castilloa* in different districts. According to Prof Preuss there were planted in the German colonies, particularly in New Guinea, about 1300 acres of *Castilloa* in 1909.

<sup>1</sup> I.R.J., 1910, vol. xxxix. p. 727.

<sup>2</sup> *Tropenpflanzer*, 1910, 14, 510-521, and *J.S.C.I.*, 1910, p. 1215.

This authority states that the cultivation of *Castilloa* is as a rule attended with more difficulties than that obtaining with other rubber trees, in spite of its rapid growth.<sup>1</sup> The method of tapping employed in New Guinea is generally that of the half herring-bone. *Castilloa* may be coagulated in a number of different ways, and such methods as precipitation with alcohol, coagulation with sulphuric acid, salt and alkalies have been tried, but the most appropriate process for the plantation appears to be that of creaming. The latex is collected in cups in the ordinary way, diluted with a considerable volume of water, stirred, strained and poured into large vessels. After a time practically the whole of the rubber collects in the form of a cream on the surface. The serum is drawn off and replaced with fresh water and the stirring and straining processes are repeated. Subsequently the rubber is washed and dried in the ordinary way.<sup>2</sup>

#### *FUNTUMIA ELASTICA*

This rubber has been planted experimentally in Uganda, in the Belgian Congo, in West Africa,<sup>3</sup> and elsewhere. A good deal has been published on the subject of *Funtumia* planting, and, on the whole, the results appear to be favourable in districts in which this tree is indigenous. The experience gained so far is, however, scarcely sufficiently extensive to enable one to state with certainty what the future of the *Funtumia* as a plantation tree is likely to be. Like *Castilloa* it possesses the advantage (over *Hevea*) of yielding a maximum of latex for a small number of tappings, an important point where labour is scarce, but the yield is relatively small and wound response is practically absent. It is probable that a maximum yield of 100 to 150 lb. per acre under good average conditions will not be exceeded.

<sup>1</sup> *I.R.J.*, Quarter-Century Number, 1909, p. 78.

<sup>2</sup> For details regarding planting, tapping, etc., see Olsson-Seffer, Russan, Ludewig, Preuss and Carruthers, *loc. cit.*

<sup>3</sup> Where it is locally known as "Lagos Silk Rubber," and by other names when prepared by native methods.



GANG OF MABIRA FOREST TAPPERS AND KIT  
(TYPES OF UGANDA LABOUR)



F. Kaye<sup>1</sup> has published in tabular form measurements of height and girth registered yearly of *Hevea*, *Castilloa* and *Funtumia* trees planted in the Botanical Gardens at Entebbe (Uganda), and the results show that the *Funtumia* trees gave the best results. Under forest conditions *Funtumia* does particularly well, and large numbers of young trees have been planted out among the old (wild) trees in the Mabira Forest.

Chevalier,<sup>2</sup> dealing with the Ivory Coast, expresses a decidedly favourable opinion regarding the future of *Funtumia*, and R. Kindt<sup>3</sup> states that the advantages of *Funtumia* are that it (in the Belgian Congo) develops normally and gives good yields in districts where relatively prolonged droughts occur. Where droughts of over four months take place, it is preferable to *Hevea*, but otherwise he regards *Hevea* and also *Manihot* as superior, particularly in regard to resistance and yield. According to Preuss,<sup>4</sup> something over 5000 acres have been planted with *Funtumia* in the German Colonies—principally in the Cameroons—and he mentions, as alternative methods of tapping, the herring-bone system and one consisting in a vertical incision along the whole length of the trunk. Interesting communications regarding culture, tapping, yields, etc., have also been published by Kinzelbach and Zimmermann,<sup>5</sup> by Kinzelbach,<sup>6</sup> by A. Schulte im Hofe,<sup>7</sup> Cuthbert Christy,<sup>8</sup> and others.

As a result of the opinions expressed by the various authorities referred to, of the experience in connexion with this tree gathered in the Middle East, and of information

<sup>1</sup> *I.R.J.*, 1910, vol. xxxix. p. 304.

<sup>2</sup> *Journal d'Agriculture des Pays Chauds*, per *I.R.J.*, 1910, vol. xxxix. p. 654.

<sup>3</sup> R. Kindt (Chef des cultures du Jardin Colonial de Laeken), *Bull. de l'Association des Planteurs de Caoutchouc*, per *G.Z.*, 1910, vol. xxiv. p. 1794.

<sup>4</sup> *Loc. cit.*

<sup>5</sup> *G.Z.*, 1909, vol. xxiii. p. 1464.

<sup>6</sup> *G.Z.*, 1909, vol. xxiv. pp. 109, 427; and 1910, p. 529.

<sup>7</sup> *G.Z.*, 1909, vol. xxiii. pp. 887, 914.

<sup>8</sup> *I.R.J.*, 1909, vol. xxxvii. p. 400.

obtained from other sources, I think it fair to conclude that *Funtumia* (like *Castilloa*, *Manihot*, and most other species excepting *Hevea*) will, in the future, be of local rather than of general importance as a plantation tree. There is, however, no question regarding the excellent quality of the rubber when prepared on the plantation system, that is to say from latex collected in an appropriate manner, and coagulated and cured on the best available lines. The pioneer work in this direction has been carried out by the Mabira Forest Company of Uganda, who have shown that it is possible to make use of the plantation system of collection, coagulation and curing for the purpose of obtaining rubber from old forest trees. There is no doubt that this system will see considerable development in the future, for it is now obvious that it is possible by means of appropriate organization to open up forest districts containing anything like a fair number of trees, to collect the latex according to a definite scheme, to bring it to central stations, and there deal with it in much the same way as is the case on the Eastern plantations. *Funtumia* latex requires an entirely different process of coagulation from that employed for *Hevea*. It is characteristic of *Funtumia* latex that it will coagulate immediately if exposed to a temperature approximating to that of boiling water, and a number of coagulating processes are based on this fact.<sup>1</sup> *Funtumia* rubber possesses peculiar and valuable properties. For purposes where great mechanical strength and moderate elasticity are required, it is, in my opinion, unsurpassed.

#### *FICUS ELASTICA (OR RAMBONG)*

*Ficus elastica* is the natural (wild) rubber tree *par excellence* of the Middle East. It has been experimentally planted to a considerable extent in Java, Sumatra, and

<sup>1</sup> For general methods of coagulation employed in various districts, cf. literature cited above.

Malaya. According to A. Berkhout, late Conservator of Forests in Java,<sup>1</sup> *Ficus* may be successfully cultivated even if planted as close as  $6\frac{1}{2} \times 6\frac{1}{2}$  feet. Indeed, he considers such close planting desirable, as weeds are thereby almost entirely kept down. From the figures which he gives regarding yield, however, it is fairly clear that *Ficus* will never be a favourite plantation tree, for according to him the yield in the 8th year per hectare (about  $2\frac{1}{2}$  acres) is no more than 44 lb., 66 lb. in the 10th year, and 176 lb. in the 20th year, results which are obviously very poor compared with *Hevea*. I have referred, in the first instance, to the data recorded by Berkhout, because the Dutch Government officials and planters have an unrivalled experience of *Ficus* and have experimented with it on a very extensive scale. The practical results obtained by them are, however, in accord with general planting experience in the British Middle Eastern districts, which has shown that while *Ficus* is a hardy tree, and produces, when it is properly prepared, rubber of good quality, it compares very unfavourably with *Hevea* in regard to yield. On the plantations which I saw in Malaya where *Ficus* trees had been cultivated, these were gradually being taken out and replaced by *Hevea*. A difficulty in regard to *Ficus elastica* latex is that it coagulates very rapidly; indeed, it is difficult to collect the latex in such a manner as to make its coagulation in bulk practicable. According to Preuss,<sup>2</sup> tapping of this tree is best carried out by making a number of oblique parallel cuts on the trunk and main branches and connecting these with the main channel. In order to prevent coagulation the latex is collected in cups containing water, and the mixture so obtained is subsequently filtered and then boiled. This process is only practicable for old trees, for with younger trees the flow of latex is so small and it coagulates so rapidly that the only practicable method is to allow the whole of the rubber to solidify in the wounds and to collect it as scrap. *Ficus* can also be coagulated by a combined process

<sup>1</sup> *Inaugural Dissertation*, Tübingen, 1909.

<sup>2</sup> *Loc. cit.*

of creaming and heating. The rubber when obtained in a cleanly fashion is of very good quality.

*MANIHOT GLAZIOVII (CEARA RUBBER)*

This tree and its congener, *Manihot dichotoma* (Jequie Manicoba), may be planted in relatively rainless districts, as it will survive a drought of from four to six months, a period which would be fatal to *Hevea*. It appears to thrive particularly well at heights of 3000 to 4000 feet. According to Preuss<sup>1</sup> and information gathered from other sources, it is tappable at a much earlier period (two to three years) than other species, and in certain districts, therefore, its cultivation offers many advantages. The tree shows "wound response," and in British Central Africa good results have been obtained with the herring-bone method, using dilute ammonia to prevent coagulation in the cuts. In this way,<sup>2</sup> over a tapping period of nine months, an average of 15 oz. per tree was obtained. In Togoland, a series of trees under six years old produced when tapped (herring-bone) over five days on the average 12 oz. of rubber, and trees barely five years old  $2\frac{3}{4}$  oz. Preuss states that single trees have yielded as much as  $12\frac{1}{2}$  lb. of rubber in a year, but considers that "only about" 275 lb. per acre (400 trees to the acre) per annum can be relied on.

R. Kindt<sup>3</sup> considers that the advantages and disadvantages of *Manihot* have been exaggerated, and gives some very interesting figures relating to results obtained in the Belgian Congo. The results recorded are selections from some of the "better and best" observed, but, on the other hand, are not maximal. The data given are on opposite page.

A writer in the *Planter's Chronicle*<sup>4</sup> is enthusiastic over the results obtained with *Ceara* on a Mysore (S. India)

<sup>1</sup> Loc. cit. p. 100.

<sup>2</sup> Loc. cit. p. 100.

<sup>3</sup> Loc. cit. p. 101.

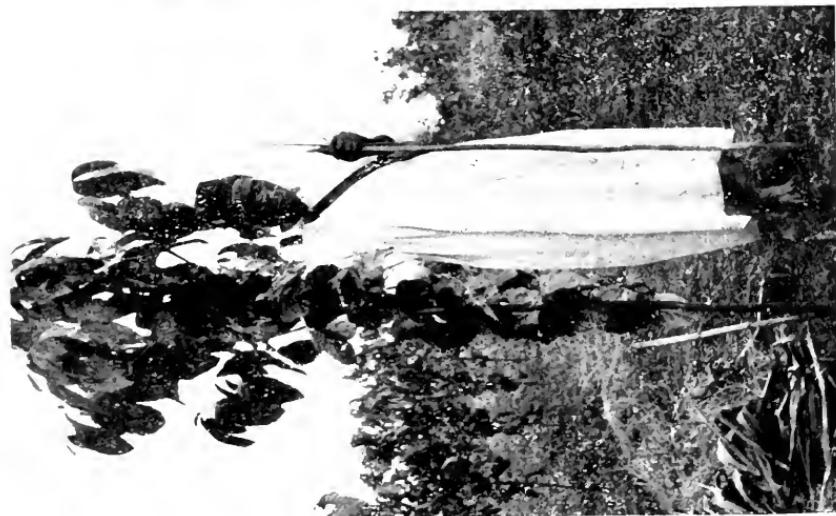
<sup>4</sup> I have not seen the original of this publication. The data are quoted from an abstract in *G.Z.*, 1910, vol. xxv. p. 17.



*CLEAR (MANHOT GLAZI)* 8 MONTHS OLD  
(CIVIL AV. GUAYAQUIL)



*FUNTUMIA ELASTICA*  
ON SODDEN SOIL IN HIGH TANOS, E.  
THE MANTA FOREST



*FUNTUMIA ELASTICA* 11 MONTHS OLD  
(CIVIL AV. GUAYAQUIL)



plantation and considers that *Manihot* may be for Mysore what *Hevea* is for Malaya. The plantation in question is situated at an altitude of about 3300 feet and the rainfall amounts to 90 to 100 inches. The dry period lasts from

#### RESULTS WITH *MANIHOT* IN THE BELGIAN CONGO

Locality.	Number of Trees.	Age.	Number of Tappings.	Dry Rubber Obtained.
Boma . . . .	3	Years 11	55	grms. <sup>1</sup> 340
" . . . .	1	12	12	625
" . . . .	10	12	43	564
Nere . . . .	10	6½	5	126
Kitobola . . . .	40	8	10	198
" . . . .	190	8	39	90 (dry season)
" . . . .	200	8	25	92 (wet season)
" . . . .	1000	8	7	42 (tapped every ten days)

October to April, and the chief rains fall during June to October. The details regarding the tappings and yields, etc., are as follow:—

#### *Results with Manihot in Mysore (S. India)*

I. *Age of trees, 3½ years.*—Number of trees tapped, 10; average girth, 13 inches; tapped on alternate days during December to February; yield of dry rubber, 4½ lb. This corresponds, taking 200 trees to the acre, to 90 lb. for six months or 180 lb. per annum.

II. *Age of trees, 5 years.*—Number of trees, 5; average girth, 12 inches; tapped as I.; yield, 5 lb. of dry rubber = 1 lb. per tree.

III. *Age of trees, 7 years.*—Number of trees, 5; average girth, 26 inches; yield, 9 lb. of dry rubber = 1.8 lb. per tree.

IV. *Age of trees, 10 years.*—Number of trees, 2; average girth, 32 inches; yield, 4.37 lb. = 2.18 lb. per tree.

<sup>1</sup> 500 grams=roughly, 1.1 lb.

V. *Age of trees, 15 years.*—Number of trees, 1; girth, 43 inches; yield, 4 lb. of dry rubber.

The trees are stated not to have suffered as a result of the tappings.

In considering the above results, which are generally favourable to *Manihot*, it must not be forgotten that the experience of planters in Ceylon and Malaya with this species has not been good, the trees showing after a few years a tendency to wither and die. It is, of course, possible that the local conditions under which it was cultivated in the Middle East were unfavourable to the plant, but whether this is so or not, one must not lose sight of the fact (and this applies to all *cultivated* species except *Hevea*) that so far there is very little practical experience regarding the yields obtainable over a number of years, and the effect of continuous tapping on the species in admittedly favourable districts.

*Manihot* when properly prepared gives a very strong product, and for tyre covers, and other articles subjected to great mechanical strain, it is probable that *Manihot* and *Funtumia elastica* cannot be surpassed.





B  
JELUTONG TREE  
SHOWING IMPROVED METHOD OF TAPPING  
(SEE P. 111)



A  
JELUTONG TREE (SARAWAK)  
SHOWING NATIVE METHOD OF TAPPING

## CHAPTER VII

### INDUSTRIAL RUBBERS

I TAKE the liberty of applying the generic term "Industrial" to rubbers—such as those obtained from the Guayule shrub and from the Jelutong tree—the preparation of which involves the application of industrial or technical methods on a wider scale than those applied to ordinary plantation or wild rubbers.

#### GUAYULE

The production of rubber from the Guayule shrub (*Parthenium argentatum*) is of particular interest to chemists and technologists, because, in the first place, the problems involved are from a technical point of view considerably more intricate than those dealing with the production of rubber from ordinary latex-bearing plants, and, secondly, because Guayule is produced on a very large scale, the amount manufactured during the year 1910 being certainly not less than 8000 to 10,000 tons, that is about 10 per cent. of the world's total rubber supply.<sup>1</sup>

<sup>1</sup> It is a little difficult to arrive at entirely reliable figures and to discriminate between bare statements and more or less official figures. H. Van der Linde (*J.S.C.I.*, 1910, p. 1284) states that Guayule would in 1910 form 20 per cent. of the world's total production of rubber of all kinds. According to the figures published in the *Bulletin de l'Association des Planteurs de Caoutchouc (G.Z.)*, 1910, xxiv. p. 1837 the chief factories in the State of Coahuila produced in the first four months of 1910 no less than 2857 tons, that is, at the rate of over 8500 tons per annum. In the fiscal year 1909–1910 the United States imported over 10,000 (long) tons of rubber from Mexico. There is reason to believe (cf. *J.S.C.I.*, 1910, p. 1215) that at least 90 per cent. of this was Guayule. According

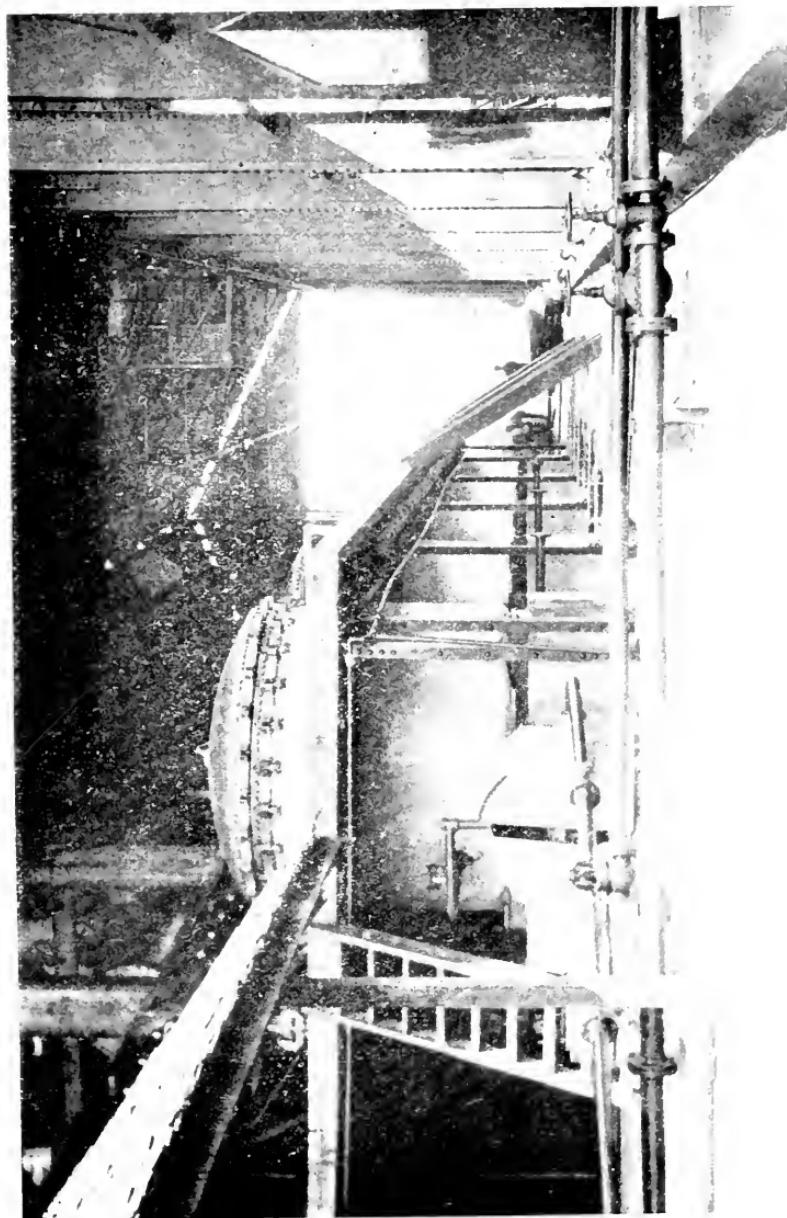
The Guayule shrub,<sup>1</sup> which prefers an altitude of 4000 to 5000 feet, occurs in a belt of territory from 1 to a 100 miles in breadth, extending roughly from Fort Stockton in Texas to the Tropic of Cancer in Mexico. In some parts of this tract it is prolific and in others it occurs only sparsely. In this shrub rubber does not occur in the form of a latex, but in solid particles dispersed through the mass of woody fibre. According to M. P. Fox<sup>2</sup> the wood contains from 6 to 18 per cent. of rubber, a similar quantity of resin, and about 10 per cent. of extractives, the residue being wood, fibre, water, and so on. The shrub is harvested either by pulling up by the roots, or preferably—in order to permit of reproduction—by cutting. It is then baled and sent to the factory. Several types of processes have been employed for obtaining the rubber from the wood, namely, chemical processes, involving the use of rubber solvents, purely mechanical processes, and mechano-chemical processes. In the latter caustic alkalis have been largely used, partly with a view to a removal of a proportion of the resin.<sup>3</sup> From the publications of F. E. Lloyd and H. Van der Linde it appears that the bulk of Guayule is prepared by purely mechanical processes, although Fox thinks a chemical process the ideal one. According to Lloyd the following type of process gives the best commercial results. The shrubs are washed, and then comminuted by special machines to an even pulp. The pulp, consisting of

to F. E. Lloyd (*I.R.W.*, New York, January 1910), 80 per cent. of the Guayule manufactured goes to the United States. Collating these data it seems probable that (in view of the rapidly increasing production and the fact that a considerable quantity is now produced in Texas) the actual production for 1910 was nearer 12,000 to 14,000 than to 10,000 tons. Seeing that the Guayule industry dates back no more than six to seven years, this is indeed a remarkable technical achievement.

<sup>1</sup> The shrub, according to Lloyd (*loc. cit.*) forms a woody, multi-branched bush, attaining at an estimated age of forty to fifty years a height of 1 metre. Mostly it is a good deal smaller than this, the average plant weighing a little over one pound.

<sup>2</sup> *I.R.J.*, Quarter-Century Number, p. 93.

<sup>3</sup> It is doubtful whether the use of caustic is desirable (cf. M. P. Fox, *I.R.J.*, January 7, 1910, vol. xxxix. p. 28).



ENTRACTORS, GOEBIL WORKS (SARAWAK)  
(SEE P. 113)



particles of rubber, wood, and other plant constituents and water, is washed into settling tanks, in which the bulk of the woody matter, etc., sinks to the bottom, the rubber together with a little bark floating on the surface. This is removed and pressed. The rubber obtained in this manner contains about 25 per cent. resin, which may be reduced to about 17 per cent. by treatment with caustic. It is again washed and then rolled, and subsequently (containing about 25 per cent. moisture) packed in sacks, or dried and pressed to blocks and exported in cases. Commercial Guayule of this type contains roughly 20 to 25 per cent. of resin calculated to dry substance, and is of a medium brown to chocolate colour. Deresinated brands (obtained from the crude product by means of resin solvents, or by a direct chemical process) are prepared for special purposes, and the best qualities—containing about 3 per cent. resin—are of a brilliant golden colour.

Guayule vulcanizes well and is a useful rubber for many purposes in low grade to medium goods.

The future of the Guayule industry is somewhat doubtful. Until quite recently it was generally believed that the plant could not be cultivated or renewed, the period of growth being too slow and cultivation from seeds impracticable. According to Lloyd, reproduction from seed may be possible in some districts but not in others. The plant, however, if cut close to the root, throws out lateral shoots, and it is to be gathered from the data recorded by Lloyd<sup>1</sup> and others (cf. *G.Z.*, 1910, vol. xxiv. p. 1341) that this growth may be sufficiently rapid for a continuation of the industry on a limited scale after the present growths have been exhausted. This, if the present rate of working continues, will have taken place about 1914-15. The writer of the article in the *Gummi Zeitung* referred to above suggests that after the old growths have been used up it will—where the method of cutting instead of uprooting has been

<sup>1</sup> Lloyd states that the renewal represents 40 per cent. of the original growth under favourable conditions.

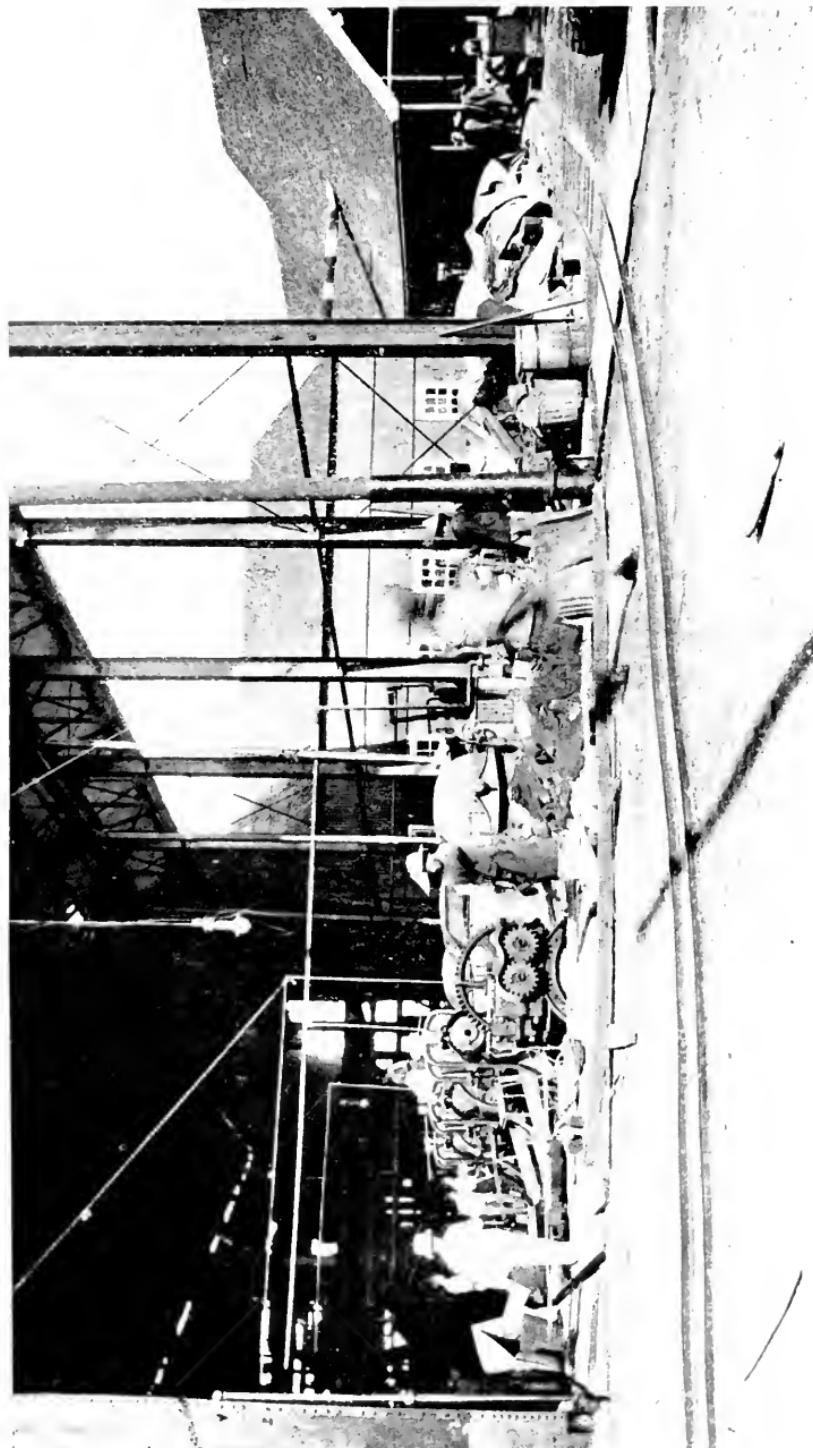
applied—be still possible to produce 2000–3000 tons where 5000 tons are now being made. It is only fair to point out, however, that Chas. P. Fox (*loc. cit.*) is of opinion that the plant is doomed, and that the renewal by lateral shoots after cutting is too slow for practical purposes. It may be that while this is true of certain regions, the views of Lloyd and Marx correctly represent what will take place in others.

The capital invested in Guayule is very large. It is computed that the capital of the main companies working in the State of Coahuila amounts to 65 million dollars (£13,000,000), of which nearly one-half is represented by a single company.

### JELUTONG RUBBER

Another type of rubber which possesses particular interest from an industrial point of view is that which is derived from Jelutong. Jelutong is obtained from a number of the *Dyera* species, the most common form being *Dyera costulata*. The tree grows to a very large size, and according to my own observations and information obtained in Sarawak and Malaya, a diameter of 4 to 6 feet is quite common for old trees. Jelutong varieties are among the commonest forest trees in Borneo, the Malay Peninsula, and Sumatra. Some idea of the quantity of raw material available will be gathered from the fact that for the year ending June 30, 1910, the United States alone imported some 23,000<sup>1</sup> tons of it. Substantially the whole of this comes from Borneo and Sumatra. As very large quantities are used in Europe, I estimate that the total production during the twelve months July 1909 to June 1910 must have been something like 40,000 tons. Furthermore, large Jelutong-bearing areas such as the Federated Malay States and parts of Borneo and Sumatra, which are undoubtedly very rich in Jelutong, have not yet been worked, and it appears probable to me that in a very short time it should be possible with proper organization to produce

<sup>1</sup> Mainly used as such in the boot and shoe industries, the manufacture of cables, etc.



PART OF INTERIOR, MAIN BUILDING, GOEBELT WORKS

(SEE P. 113)



annually some 60,000 to 70,000 tons of this raw material. Different qualities of Jelutong are known in the trade, according to the districts from which they are derived, as Palembang (Sumatra), Pontianac or Dead Borneo (South Borneo), Sarawak, and so on. Commercial Jelutong is obtained by coagulating the latex derived from the Jelutong tree, and in this respect, therefore, the preparation of Jelutong rubber resembles the process by which ordinary rubber varieties are obtained. The Jelutong tree is generally tapped by the natives in one of two ways, which resemble the full spiral and V system employed on plantation species respectively (see Plate XXIII. *A*). A more rational system of tapping has now been introduced on some areas, and this consists in cutting a long V, a central channel running from the point of the V to the collecting cup. The V cuts may be from 6 to 8 feet or more in length, and are made by means of a species of gouge attached to the end of a sturdy bamboo<sup>1</sup> (see Plate XXIII. *B*). The Jelutong tree yields large quantities of latex ; thus a number of trees which were tapped under the supervision of the Department of Forests, F.M.S., gave the following figures :—

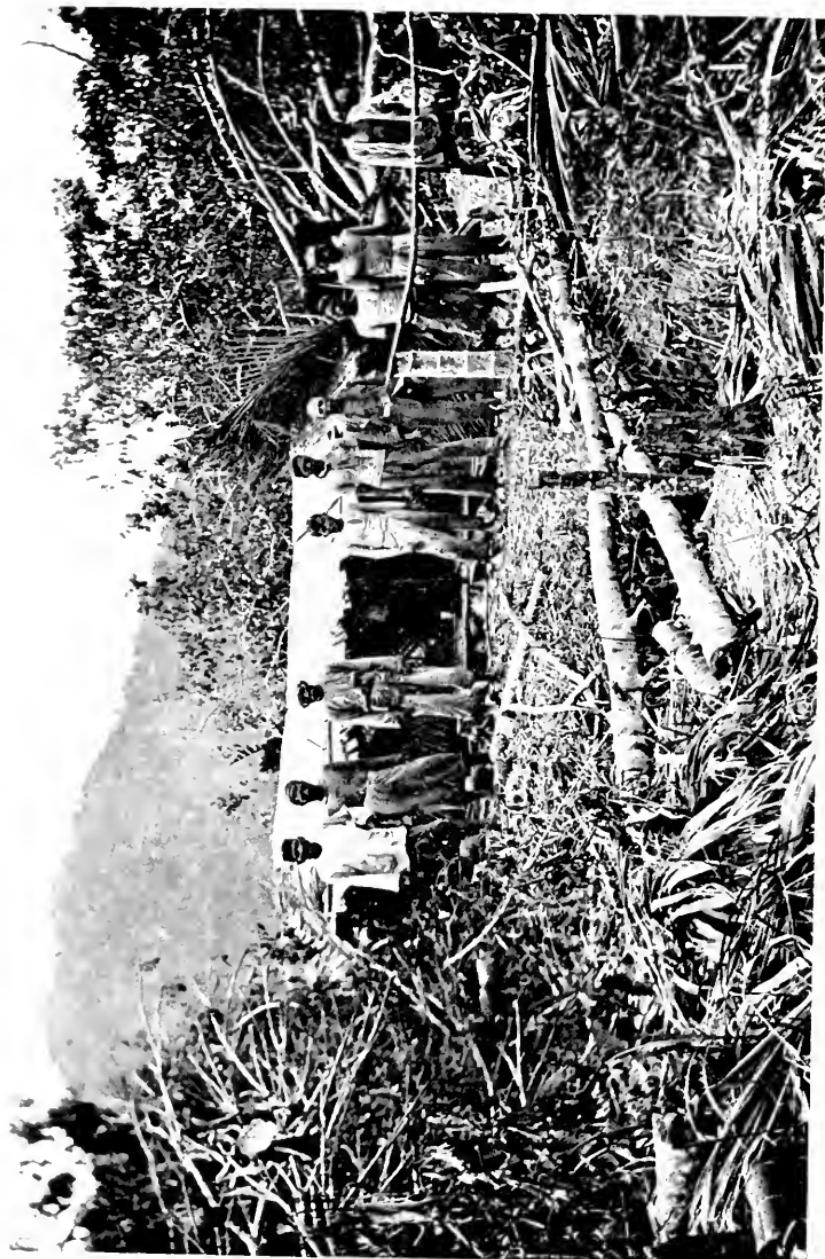
First tapping . . . .	48	trees yielded	56	catties. <sup>2</sup>
Second „ . . . .	32	„ „	66	„

These tappings were carried out during the month of December 1909. It will be seen that the second tappings give a considerably higher yield than the first. This, it appears, is partly due to wound response, but another reason, which my own observations have confirmed, is that the somewhat sluggish primary yield is largely due to the fact that the latex at the first tapping is very thick, tends to coagulate in the cuts, and so prevents further flow. This phenomenon gradually disappears as the tappings are repeated. Experi-

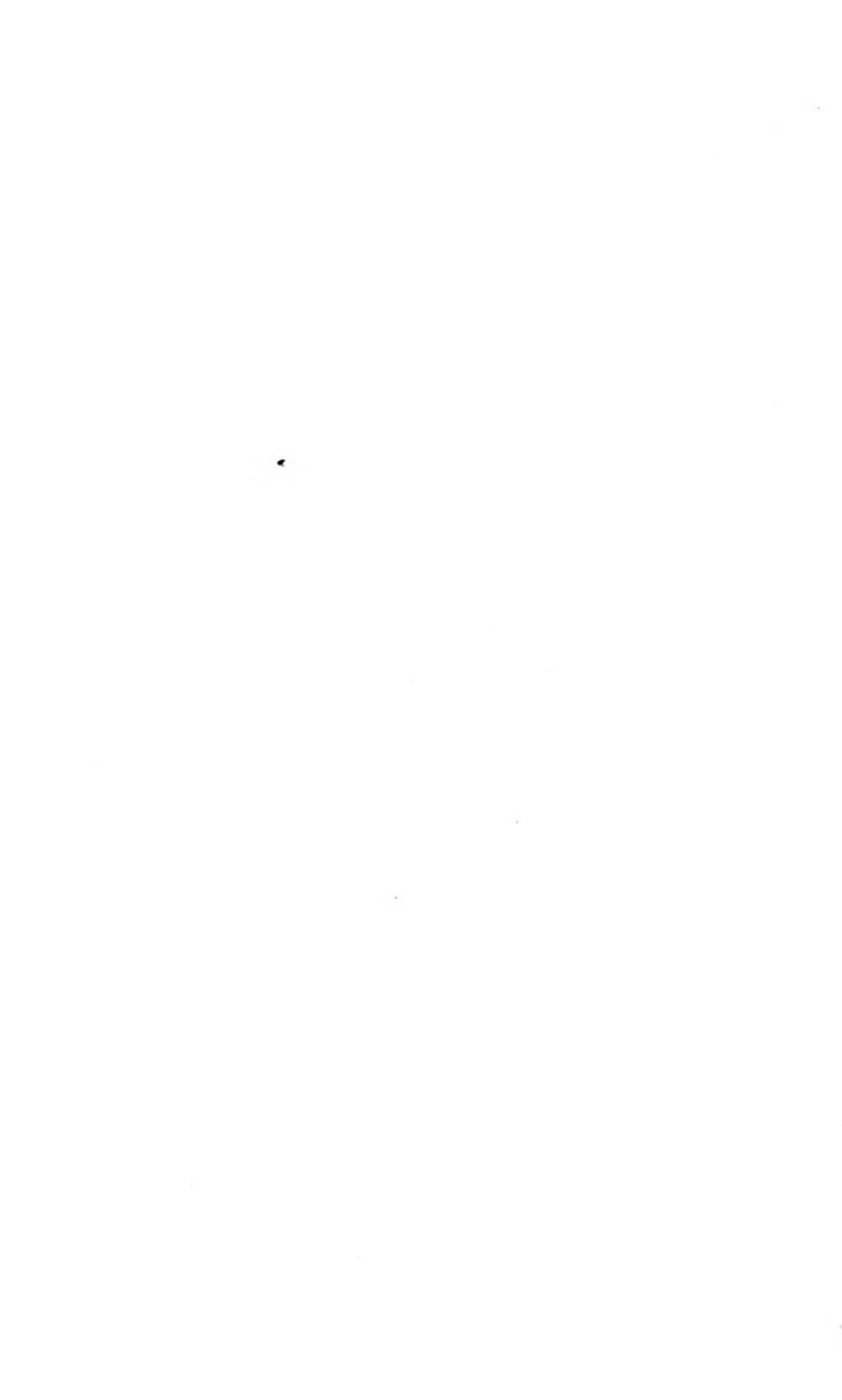
<sup>1</sup> This system was devised by J. L. Elliot, the founder of an industrial large scale enterprise for the production of high grade rubber from the low grade raw material.

<sup>2</sup> The catty = 1.33 lb.

ments have shown that a tree may be tapped at least forty times annually without injury, and on this basis a mature tree should yield about 100 lb. of latex per annum. The latex is very rich in solids, particularly in some districts in Malaya, and on the average yields about 60 to 70 per cent. of solid (wet) Jelutong. The latter contains roughly 10 per cent. of rubber. For the coagulation of the latex the natives employ a number of curious mixtures, generally including kerosene oil on the one hand and a number of "powders" on the other. The latter are sold to them by Chinese dealers, and some of these which I came across in Borneo are of very little value for the purpose intended. The principal ingredients of these "powders" are copper sulphate, alum, gypsum, etc. The native method consists in adding some of the kerosene and a little of the "powder" and stirring the whole vigorously. Then a little kerosene and powder alternately are gradually added until the whole of the latex sets to a more or less firm block. It is surprising that this crude method of coagulation produces material from which, nevertheless, very fair rubber can be extracted. It is, however, equally certain that by improved methods of coagulation much better rubber can be obtained. Mr. G. A. Morton, the chief chemist to the United Malaysian Rubber Company, has recently made a thorough study of methods of coagulating Jelutong latex, and has succeeded in devising a method which produces rubber which in appearance and general quality appears to be indistinguishable from the very highest class of plantation *Hevea*, namely, a light amber, strong, clean, smoked crêpe of close texture. Commercial Jelutong comes into the market in the form of large, almost white, balls or blocks, weighing about 30 to 50 lb. When fresh it is of a stiff cheesy constituency, and in this state contains roughly 60 to 70 per cent. of water, the balance consisting mainly of resin. It was formerly believed that the rubber in Jelutong was not a true but a pseudo-rubber, but I am satisfied, as a result of the examination of the physical properties of the crude rubber, and of vulcanization



TYPE'S OF MAI AV LABOUR  
COMMENCEMENT OF CLEARING FOR UNITED MALAYSIAN CO.'S WORKS ON KAKIMON ISLAND, NEAR SINGAPORE.



experiments conducted with it, that there is no reason for this statement. The origin of the view that Jelutong rubber is not a true rubber was probably due to the fact that most of it has hitherto been prepared by methods which have failed to separate from the raw material certain substances which exercise a deleterious influence on its stability and vulcanizing capacity. As a matter of fact, the rubber in Jelutong is of a very high grade, and when properly prepared comparable to other high-class rubbers. At the Goebilt (Sarawak) works of the United Malaysian Rubber Company, which I inspected in May 1910, the main operations—as some of the features of the process are of a secret character I obviously cannot enter into details—are as follows:—The Jelutong is subjected to a preliminary purification with a view to removing dirt, mechanical impurities, etc., and is then extracted with a suitable resin solvent. After the removal of the solvent the rubber contained in the extractors—now in a dry and comparatively pure condition—is subjected to a final process of purification, and is then dried and “smoke” cured (see Plates XXIV. and XXV.). It is shipped mainly in the form of crêpe, in cases. The main difficulties with deresinating processes hitherto have been (*a*) the loss of solvent has been very high—as much as 2 to 3 lb. per pound of rubber produced, and (*b*) owing to the imperfect forms of treatment and purification the quality of the rubber has been very poor, with a pronounced tendency to tackiness. Both these difficulties have been overcome very ingeniously in the process referred to above. The loss of solvent was estimated by me over a period of eight days at 0.3 lb. per pound of rubber and the quality of the rubber obtainable has already been referred to.

With regard to the production of rubber that may be expected from this source, I may say that the Goebilt works were designed to produce 10,000 lb. of finished rubber per day, and that new works in course of erection on Karimon Island (close to Singapore) will have treble this capacity. The supply of raw material appears to be adequately assured.

## RUBBER FROM VINES AND BARK

In tropical Africa, in Madagascar, and other parts of the world there are immense districts abounding with rubber vines and creepers. Native methods for obtaining rubber from these plants generally consist in cutting them down

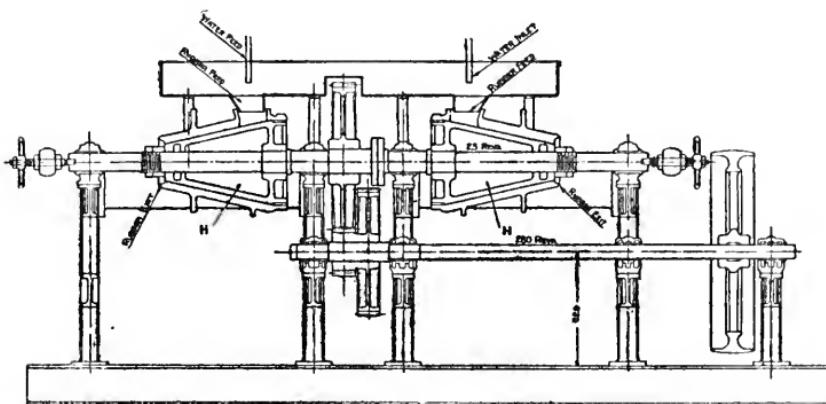


FIG. 2 A.—Guiguet Machine  
For mechanically separating Rubber from Bark (see p. 115)

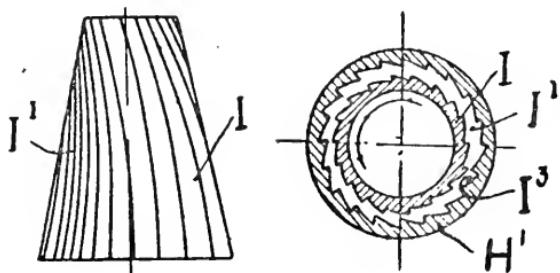


FIG. 2 B.—Essential parts of the Guiguet "Agglomerator" (II Fig. 2 A.)

and tapping or "bleeding" them until the latex ceases to flow. This method is wasteful as it cannot be applied to small vines or branches, and, inasmuch as the bark of rubber vines is as a rule relatively thick, a great deal of latex remains in it after all visible flow from the cuts ceases. If this bark is stripped and allowed to dry, the latex rapidly

coagulates, and the rubber can then be extracted by mechanical means on the same principles as those employed on the plantation for bark scrap (see "Plantation Industry," p. 78). The designing of efficient machinery for this purpose has made considerable strides during recent times, and as a result, large tracts of country are being opened up principally in Madagascar and in the continent of Africa, with a view to extracting vine rubber in a methodical manner. Districts rich in vines are selected, and in these suitable machinery is erected. It is proposed to utilize the areas cleared of vines for replanting, so assuring a continuous supply of raw material. The pioneer in this type of enterprise was the Madagascar Rubber Company Ltd., and the machine employed by it and some other companies is the Guiguet (called after its designer), the essential parts of which are shown in Figs. 2 A and 2 B, p. 114. The *modus operandi* is briefly as follows:—The bark, after stripping, is fed into a hopper and is then crushed in the presence of water to a paste by means of a device consisting of a fixed and a rotatory plate, each provided with teeth.<sup>1</sup> The paste so obtained is carried by a stream of water to the essential part of the mechanism the "agglomerators" (H). The latter each comprise a cone (I) provided with helicoidal grooves ( $I^1$ ) of a shape similar to ratchet teeth. These cones rotate within conical sleeves ( $H^1$ ) provided with similarly formed grooves ( $I^3$ ). The helices of grooves  $I^3$  are of opposite sign to those of  $I^1$ . The water circulating between the cones and sleeves carries away the bulk of the bark, woody fibre, etc., whilst the rubber particles which are softened by the friction or artificially applied heat, agglomerate and pass out in the manner indicated in Fig. 2 A in the shape of irregular, wormlike masses. From the agglomerator the products pass through a trough to a rotating drum in which a further separation of rubber from finely divided bark, etc., takes place. Finally, the rubber passes to another agglomerator, where it is still further purified and shaped into rather larger (irregular) masses.

<sup>1</sup> This part of the machine is not shown in the illustration.

## CHAPTER VIII

### RUBBER LATICES AND COAGULATION

#### CHEMICAL AND PHYSICAL PROPERTIES OF RUBBER LATICES

IT is desirable to draw attention to the fact that latices from different trees vary considerably—I refer to the main species, and not to very resinous or abnormal latices—in regard to their chemical and physical properties. That this should be so appears *a priori* to be likely rather than unlikely, and I might well have omitted to emphasize this fact had it not been within my own experience and that of others that much time, labour and capital have been wasted in the past by those who have overlooked or neglected to take into consideration this somewhat obvious cardinal principle. It should therefore be remembered that the experimental data recorded in the literature of this subject must always be regarded from this point of view, and the same applies to practical experience in the field or curing-house.

#### PHYSICAL PROPERTIES OF RUBBER LATICES

Under the microscope rubber latex is seen to consist of a fluid or serum in which innumerable particles of a globular shape are suspended. These particles show typical and active "Brownian" movement. If an electric current is passed through the latex (*Hevea* or *Funtumia*) the area round the negative pole clears and the globules wander to the

positive pole, there forming a coagulum. Latex may therefore be regarded as a negative colloidal emulsion, the surface of the particles carrying a — electrical charge.

*Size of Globules.*—The size of the globules varies considerably according to the species, but also in the same species. Thus Henri<sup>1</sup> states that the particles in *Hevea* latex examined by him varied from 0.5 to 2 $\mu$ , and Spence<sup>1</sup> refers to 2 $\mu$  as an average figure. The age of the trees from which the latex is obtained appears to be a factor in this connexion, for I have observed that the globules in latex from a very young plant (*Hevea*) had a diameter of about 0.5 $\mu$ , whereas the globules in older latices averaged 1 to 2 $\mu$ . This observation is in accordance with the well-known fact that it is generally difficult to coagulate young latices or latices which (such as *Funtumia*<sup>2</sup>) normally contain relatively small globules. Fickendey<sup>3</sup> investigated a number of latices in this connexion with the following results:—

Tree.	Size of Globules.
<i>Hevea brasiliensis</i> . . . . .	0.5-1 $\mu$
<i>Ficus elastica</i> . . . . .	2-3,,
<i>Castilla elastica</i> . . . . .	2-3,,
<i>Sapium</i> , spec. . . . .	0.5-4,, (mostly 2-3 $\mu$ ).

*Modification and Cessation of Brownian Movement.*—By the addition of chemical reagents (acids or alkalis, salts, etc.) by dilution, by boiling, or by the action of the electric current, the Brownian movement is more or less (according to the nature of the latex, the quantity of the reagents, etc.) profoundly modified. It may be merely slowed or caused to cease altogether. This cessation may be either temporary or permanent, or, in more scientific language, a *reversible* or *irreversible* colloidal gel forms. V. Henri<sup>4</sup> has shown that in the case of dialysed *Hevea* latex, an alkaline medium *plus*

<sup>1</sup> Cf. V. Henri, *Compt. rend.*, 1907, cxliv. 431-433, and Spence, *I.R.J.*, 1908, vol. xxxvi. pp. 233-234.

<sup>2</sup> Spence, *loc. cit.*

<sup>3</sup> *Tropenfplanzen*, 1909, 5, and *G.Z.*, 1909, vol. xxiv. p. 12.

<sup>4</sup> *Lectures*, p. 205.

salts of di- and tri-valent metals produces merely *agglutination* or coalescence, the globules running together to form irregular masses, which may, by shaking or by dilution, be evenly re-distributed throughout the liquid. If an acid medium or other reagents such as alcohol or acetone are employed, the globules unite to form a reticulated structure, which proves to be an *irreversible gel*, that is, a mass which cannot be re-suspended or dissolved in the medium from which it was derived. This phenomenon represents true coagulation.

Henri (*loc. cit.*) by means of cinematographic measurements was able to show that in a *Hevea* latex (dialysed) diluted to contain 20 globules in the field, the average displacement of a globule in one-twentieth of a second was as follows :—

(1) Pure latex . . . . .	0.62 $\mu$
(2) With an alkali added . . . . .	0.31 ,,, (slowing only, no coalescence)
(3) Very small quantity of acid . . . . .	0.07 ,,,

The quantity of acid added in (3) was just short of the amount necessary to produce incipient coagulation. The effect was a practical cessation of movement.

Henri suggests as an explanation of these phenomena, that each globule is surrounded by a zone of adsorption in which (for instance) the acid added is more concentrated than in the intervening liquid.

*Protective Colloids in Latex.*—The various methods employed for producing coalescence or coagulation, that is modification of Brownian movement, in latices, correspond generally to the well-known methods for producing changes of specific surface and other alterations in colloidal solutions generally. It is therefore pertinent to inquire whether some or any of the factors which tend to promote the formation or stability of suspensoids or emulsoids in general are not responsible for the relative stability of rubber latices. Fickendey (*loc. cit.*) suggests that protective colloids probably play a rôle in keeping the globules in suspension,

and refers to the fact that *Hevea* and other latices which are coagulated by proteid precipitants contain proteid. *Funtumia*, according to the same writer, contains no proteid, but contains a dialysable protective agent, which, according to him, is a peptone. *Funtumia* is coagulated by peptone reagents (according to Fickendey), but its stability to other reagents is not due merely to the smallness of the globules, but to the absence of proteid.

*Specific Gravity*.—Various observers give the range (for normal latices) for *Hevea* as from 0.973 to 0.979, and Stevens and Beadle give 0.975 as representative for *Ficus elastica*.

### *Constituents of Rubber Latices*

In addition to the constituents which are well known or have already been referred to, such as rubber, resins, proteid, peptones and mineral constituents,<sup>1</sup> rubber latices have been found to contain various sugars, simple oxygen derivatives, and a number of enzymes.

*The Sugars* are of considerable interest, not only from a scientific, but also from a technical point of view, inasmuch as there is reason to believe that the inferiority and inclination to tackiness of certain rubbers is at least partly due to the presence of these substances in, or rather their non-removal from, the crude product. Girard isolated three distinct sugars from Gaboon Ball, Borneo rubber and Madagascar rubber respectively. The first of these, called by him Dambonite,<sup>2</sup> was identified by Maquenne<sup>3</sup> as dimethyl - i - inosite. The second, Bornesite,<sup>4</sup> was found to be a mono - methyl - inosite. This was confirmed by

<sup>1</sup> For resins, see pp. 139, 251; mineral matter, pp. 123, 253, and Weber, *B.*, 1903, 3108-3115; Tromp de Haas, *B.*, 1904, 3298-3301; Spence, *Liverpool University, Inst. Tropical Research*, Reprints Nos. 9 and 19; Fickendey, *loc. cit.*; etc.

<sup>2</sup> *Compt. rend.*, 1873, tome Ixxvii. pp. 820-873. Cf. also Ditmar, *Die Analyse des Kautschuks* (Hartleben, Vienna, 1909), p. 23; and Muspratt, 1893, vol. iv. p. 1064.

<sup>3</sup> *Ann. de chim. et phys.*, 1887 (6) 12, p. 566; cf. also Ditmar, *loc. cit.*

<sup>4</sup> *Compt. rend.*, 1873, tome Ixxvii. p. 995.

Flint and Tollens.<sup>1</sup> The third Matezite,<sup>2</sup>  $C_{10}H_{20}O_9$ , splits off a methyl group on treatment with hydriodic acid, forming Matezo Dambose or (as Dambose is i-inosite)  $C_3H_6O_3 \cdot C_6H_{12}O_6$ .

*Simple Oxygen Derivatives.*—Harries<sup>3</sup> found in *Ficus elastica* and in *Ficus magnolooides Borci* two albane-like crystalline substances to which he assigned the formulæ  $(C_{10}H_{16}O)_2$  and  $(C_{10}H_{16}O)_3$ , respectively.

*Enzymes.*—Rubber latices, like most plant juices, contain a number of enzymes, which are of considerable importance both from a scientific and technical standpoint. It has been shown by Bamber<sup>4</sup> that the darkening of *Hevea* rubber may be prevented by employing a method of coagulation involving the use of heat, or by immersing the rubber, immediately after coagulation, in water kept at a temperature (in practice 180° F.) at which the oxidizing enzyme is destroyed. Bamber also observed that “by quick coagulation (especially in the dark), careful skimming to remove froth and a resin that rises and discolours quickly, and thorough washing, a certain proportion of each day's make can be made colourless without the aid of heat. . . .” (the italics are mine). That is to say, the enzyme may be washed out. This is in consonance with the experiments of Spence,<sup>5</sup> who showed that *Funtumia elastica* rubber (which shows a very marked propensity to darken) may be obtained almost colourless by “creaming” repeatedly with large quantities of water. The removal of the enzyme (shown definitely by Spence to be an oxydase) coincided with the practical disappearance of proteid from the rubber, and Spence argues from this, and from the fact that samples prepared by any of the usual methods of coagulation in which the proteid is afterwards to be found in the rubber clot, darken rapidly in colour, that there is an intimate

<sup>1</sup> *Lieb. Annalen.*, 272, 1893, p. 289.

<sup>2</sup> *Compt. rend.*, 1896, tome cx. pp. 46, 84.

<sup>3</sup> *B.*, 1904, 2842-2848.

<sup>4</sup> *Lectures*, p. 73.

<sup>5</sup> *Bio-chemical Journal*, 1908, vol. ii., 4, p. 178.

association between the enzyme and the proteid matter.<sup>1</sup> Spence<sup>2</sup> has further shown that *Hevea* latex contains both an oxydase and a per-oxydase. The former appears to be readily destroyed, for on examining (unwashed Brazilian) Para he<sup>3</sup> was able to isolate only the peroxydase.

V. Cayla<sup>4</sup> examined a series of latices and found evidence of the presence of oxydase, peroxydase, and catalase.

### *General Composition of Latices*

The rubber content—and this refers also to some of the other constituents, particularly the resin—of latices varies within wide limits according to the age of the trees, tapping height, the district, and so on. In conjunction with F. Kaye I<sup>5</sup> investigated an extreme case of considerable interest. The latex was obtained by normal tapping from the upper<sup>6</sup> bark of a 5 year old *Hevea* (Ceylon), and was found to contain no more than 4.6 per cent. of crude rubber. An analysis of the latter gave the following results:—

	Per cent.
Moisture . . . . .	3.27
Resin . . . . .	4.19
Ash . . . . .	2.25
Nitrogen . . . . .	0.41

<sup>1</sup> I have in the course of some work on *Funtumia* latex made observations which lead me to think that the darkening is not entirely due to enzymic influence, but that certain water soluble (apparently non-nitrogenous) readily oxidizable substances are of moment in this connexion. It is also certain that the enzyme associated with colour formation in *Funtumia* is not a simple oxydase, for freshly coagulated *Funtumia* rubber may be exposed to the action of boiling water for prolonged periods without affecting the subsequent darkening. Spence suggests that this may be accounted for by assuming that the oxydase is present in the form of a zymogen.

<sup>2</sup> *Loc. cit.*, vol. iii. p. 351.

<sup>3</sup> *Bio-chemical Journal*, 1908, vol. ii., 4, p. 178.

<sup>4</sup> *G.Z.*, 1908, vol. xxiii. p. 213.

<sup>5</sup> *I.R.J.*, 1907, vol. xxxiv. p. 24, and *J.S.C.I.*, 1907, p. 935.

<sup>6</sup> Adriani (*Jahresber. Fortsch. d. Chem.*, 1850, p. 519) noticed that the upper bark of *Ficus elastica* contained more water and less rubber than the lower bark. This has since been observed on numerous occasions in *Hevea*.

## RUBBER

The clear serum showed 0.05 per cent. of solids and was free from sugar and glucosides, and it was found that about two-thirds of the total nitrogen had passed into the rubber. Normally, *Hevea* latex from mature, sound trees contains 30 to 40 per cent. of dry rubber.

The following may be regarded as typical examples of various latices:—

*HEVEA BRASILIENSIS LATICES*

	Ceylon Latices. <sup>1</sup>		Malay Latices. <sup>2</sup>	
	A. Per cent.	B. Per cent.	Four Year Old Trees.	Ten Year Old Trees.
Rubber . . .	41.29	32.00	27.07	35.62
Resin . . .	...	2.03	1.22	1.65
I'roteid . . .	2.18	2.03	1.47	2.03
Mineral matter . .	0.41	...	0.24	0.70
Sugars . . .	0.36	...	...	...
Water . . .	55.15	55.56	70.00	60.00

In latices C and D Beadle and Stevens found no more than a trace of reducing sugars, but after inversion C showed 0.79 per cent. (calculated as glucose) and D 0.34 per cent. The latices (C and D) were mixed products of at least one hundred trees, collected in dry weather and unmixed with water.

*FUNTUMIA ELASTICA (CAMEROONS)<sup>3</sup>*

	Per cent.
Specific Gravity @ 25 °C. . . . .	0.979-0.988
Water . . . . .	47.68
Ash . . . . .	0.99
Lead acetate precipitate . . . . .	1.98
Peptones . . . . .	3.25
Rubber . . . . .	40.72
Resin . . . . .	4.46

<sup>1</sup> Kelway Bamber, *Circular, R.B.G.*, June 1899, per Herbert Wright, *loc. cit.*

<sup>2</sup> Beadle and Stevens, *Analyst*, 1911, p. 8.

<sup>3</sup> Fickendey, *Tropenpflanzen*, 1909, No. 5.

This latex (which according to my experience may be regarded as normal) was gathered during the dry season, and was faintly acid. No proteid, sugar, starch or oxydase could be found. The ash contained 39.41 per cent. MgO, 4.20 per cent. CaO, 17.02 per cent. SO<sub>3</sub>, 5.42 per cent. Cl, 5.67 per cent. P<sub>2</sub>O<sub>5</sub>, and small quantities of alumina and alkalis.

Spence<sup>1</sup> has published an interesting *Funtumia elastica* analysis, but the latex to which this refers was obviously somewhat abnormal. The rubber content was only 19.85 per cent., whereas, according to numerous determinations made by myself, normal mature *Funtumia* latex contains at least 35 to 40 per cent. Spence determined (by dialysis) the "organic crystalloids," finding 1.39 per cent.; insoluble constituents (mostly proteid) 0.36 per cent.; total nitrogen 0.438 per cent.; total ash (of which 0.21 per cent. was potassium in the form of soluble salts) 0.266 per cent.

The following are analyses of *Ficus elastica* and *Castilloa elastica* latices from the Malay Peninsula by Beadle and Stevens.<sup>2</sup> Both latices were from 8 year old trees:—

	<i>Ficus Elastica Latex.</i>	<i>Castilloa Elastica Latex.</i>
Rubber . . . . .	Per cent.	Per cent.
Resin . . . . .	37.3	31.2
Proteid . . . . .	2.4	5.0
Ash . . . . .	0.4	0.2
Water . . . . .	0.4	0.9
	59.5	62.7

### COAGULATION

The coagulation of a rubber latex involves physical and perhaps also chemical changes of a very complex nature. It is not possible to offer any simple explanation o

<sup>1</sup> *Q.J. Reprints*, 1907, No. 9, and *J.S.C.I.*, 1907, p. 1020

<sup>2</sup> *Lectures*, pp. 231 et seq.

coagulation phenomena, or to sum up in a single phrase—as has frequently been attempted—the action and effect of the various factors which play a rôle in the process. It has been suggested by Spence<sup>1</sup> that coagulation is due to the disturbance of the equilibrium between two opposite forces, namely, (*a*) the negative electrical charge on the colloid aggregate, and (*b*) the surface tension of the particles, but although this explanation is probably correct so far as it goes, it merely indicates an ultimate condition, but is silent as to the complicated factors by which this condition is brought about. I have found it very helpful, with a view to obtaining some insight into the mechanism of coagulation of a specific latex, and also from the standpoint of applying the inferences to be gleaned by this method to practical problems, to consider rubber latex not as a thing apart, but merely as a particular example of colloidal emulsoids. Weber<sup>2</sup> considered that the rubber globules consist of a proteid sheath containing a liquid diterpene, and that the process of coagulation involves the bursting of the proteid sheath and the subsequent polymerization of the contained liquid to rubber.

Weber's theory was based mainly on the following: (*a*) From fresh (*Castilloa*) latex a substance could be extracted by means of ether, which, although at first weak and inelastic, became, if pressed, converted into rubber. According to Weber, rubber is not soluble in ether, and therefore the globules do not consist of, or contain, rubber as such. (*b*) By compressing a drop of latex between a cover glass and slide, the globules are seen to burst and a liquid exudes from them. With regard to (*b*), I think that there can be no doubt that Weber's statement was based on an error of observation pure and simple. With regard to the remainder of Weber's theory, Tromp de Haas and de Jong<sup>3</sup> showed that proteid precipitants do not coagulate *Castilloa* latex, neither does the removal of the proteid from the latex bring about coagulation. They also

<sup>1</sup> *Q. J. Reprints*, 1907, No. 9, pp. 3-10.      <sup>2</sup> *B.*, 1903, 36, 3108 *et seq.*

<sup>3</sup> *B.*, 1904, 7, 3298.

showed that freshly coagulated rubber is by no means insoluble in ether. Spence<sup>1</sup> has confirmed Tromp de Haas and de Jong in regard to the proteid, by showing that if (*Funtumia*) latex is digested with proteolysts (such as trypsin), coagulation is not brought about. This one would expect to be the case if the globules were surrounded by a proteid sheath. The solubility of rubber in ether has formed the subject of some interesting work by Harries.<sup>2</sup> He found that if rubber is freshly coagulated or precipitated—for instance by precipitating by means of alcohol from a solution in a rubber solvent—the coagulum is soluble in ether. This modification of rubber he called *a*. The latter gradually passes (on standing or if mechanically worked) into modification *b* which is insoluble in ether. The third modification—termed rubber *c* by Harries—which is of an oily nature, may be obtained by exposing a rubber solution to sunlight and heat. Modification *b* may be transformed into *a* by boiling with acetic anhydride. A further point against Weber's theory is that Henri's<sup>3</sup> physical measurements point to a substance of high molecular weight, and Hinrichsen's<sup>4</sup> molecular weight determination—although by no means conclusive—are confirmatory. In recent times, however, absolute proof of the erroneous character of Weber's view has been forthcoming. V. Henri,<sup>5</sup> to whose work I have already referred, in a series of brilliant experiments has demonstrated—by means of micro-photographs and by micro-cinematography—exactly how the globules behave during coagulation, and has shown that, according to the method of coagulation, the globules form a reticular network of varying pattern, the lines of the network consisting of rows and groups of globules at rest. Henri worked with *Hevea* latex, but I have had numerous opportunities of making similar observations on *Funtumia*. To carry the

<sup>1</sup> *Q. J. Reprints*, 1907, No. 9, p. 5.

<sup>2</sup> *B.*, 1904, 37, 3842; and *G.Z.*, 1910, vol. xxiv. p. 851.

<sup>3</sup> *Compt. rend.*, 1907, tome cxliv. p. 433; and *J.S.C.I.*, 1907, p. 264.

<sup>4</sup> *B.*, 1909, 42, 4329.

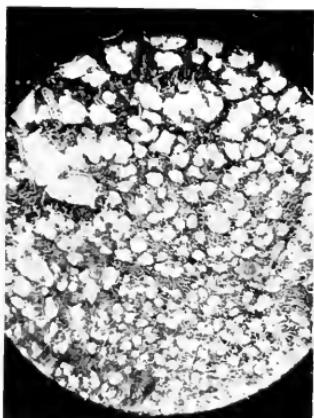
<sup>5</sup> *Lectures*, 203.

proof of the continued existence of the globules a step further, I have been able to prove<sup>1</sup> that they may be readily observed in dry transparent rubber, and that they persist in rubber solutions made by dissolving dry rubber in a solvent.<sup>2</sup>

*Modification of Structure.*—Weber observed that if freshly coagulated rubber is mechanically worked (*e.g.* by rolling) heat is evolved, and it changes from a soft, cheesy mass to a firm, elastic substance. No doubt every one who has worked with rubber latex has made the latter observation, but the explanation suggested by Weber of the cause of this change in state, namely, that it is due to "polymerization," is purely hypothetical. While there is nothing to support this theory, I have made an observation which appears to explain the phenomenon referred to in a simple manner. I coagulated—by means of heat—a drop of *Funtumia elastica* between a slide and cover glass, and observed that the coagulum exhibited a fairly fine reticular structure, similar in character to the structure observed in other cases by Henri (*loc. cit.*) and myself (see Plate XXVII. *A*). I then moved the cover glass slightly backwards and forwards in a lateral direction, applying slight pressure at the same time, and, on re-examining the film under the microscope, found that it had *completely* altered its structure. The fine reticular structure was gone, and in its place was a relatively coarse, large-meshed pattern (Plate XXVII. *B*). This had evidently been formed by a purely mechanical re-arrangement of the fine threads of the original structure, and such a mechanical re-arrangement would in all probability involve the production or absorption of heat. The difference between the original and final structures readily explains the difference in the physical characteristics of the two.

<sup>1</sup> Schidrowitz, "The Structure of Crude Rubber," *J.S.C.I.*, 1909, p. 6.

<sup>2</sup> See p. 152, and Plate XXVII. *C*.



A

MICRO-PHOTOGRAPH OF  
A DROP OF FRESHLY CO-  
AGULATED FUNT. ELAST.  
LATEX, SHOWING RETI-  
CULAR STRUCTURE

(SEE P. 126)

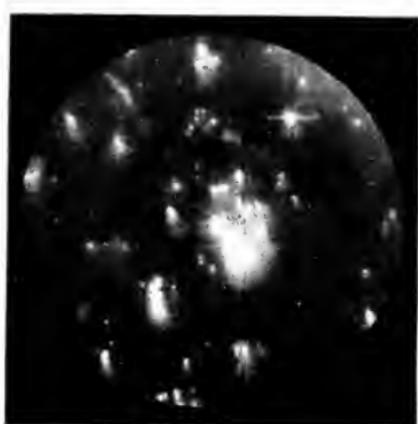


B

THE SAME AS "A" AFTER APPLY-  
ING PRESSURE. NOTE THE AL-  
TERATION IN STRUCTURE

FROM A DRAWING

(SEE P. 126)



C

ULTRA-MICRO-PHOTOGRAPH OF A  
SOLUTION OF RUBBER IN BENZENE

(SEE P. 126)



*Influence of the Method of Coagulation on Quality*

From the discussion on the methods of coagulation of plantation rubber and from the data regarding the mechanism of coagulation given, the reader will have gathered that the method of coagulation is likely to have an important influence on the nature of the rubber produced. In dealing with a new latex, or if it is desired to modify the method of coagulation in use with a well-known latex, the following general methods may be considered :—

1. *Para Method*.—Coagulation and curing by direct heat in one operation.
2. *Coagulation by Heating or Boiling*.—Of the undiluted or diluted latex with or without the addition of chemical reagents. The reagents added may be utilized merely as coagulants or with a view to stabilizing the rubber subsequently (antiseptics).
3. *Coagulation in the Cold*.—(a) By diluting only with water—*creaming*. (b) By the addition of chemical reagents to the undiluted or diluted latex. The reagents may be merely coagulants or may also (or in part) play the rôle of antiseptics. With regard to the reagents, that may be from a practical point of view first considered (and this applies, of course, to the hot processes as well), these are *various acids* (acetic, tannic, tartaric, formic, hydrofluoric acids, etc.), *phenols*, and, in a few cases, *formaldehyde*. Alkalies are, as a rule, either anti-coagulants (preservatives) or unsatisfactory.
4. *Mechanical Methods*.—Churning, centrifuging (alone or after adding chemical reagents or diluting), collection as bark scrap and separation by purely mechanical means.

Many native methods, for instance coagulation by smearing the latex on the skin and peeling off the film of rubber

after the heat of the body has caused the water to evaporate (Congo and elsewhere), are interesting but of little practical import, and I therefore refrain from entering into further details in this connexion.<sup>1</sup>

One of the most interesting instances of the influence of the coagulant on quality is that afforded by the action of formaldehyde on *Funtumia elastica* latex.<sup>2</sup> While formaldehyde is a preservative for most latices, it acts as a coagulant towards the latex referred to, and produces a rubber of most extraordinary quality. The elasticity (as compared with the rubber obtained by normal *Funtumia* coagulation methods) is much impaired, but a remarkable toughness is produced, an effect, indeed, which is quite unique in my experience.

V. Henri<sup>3</sup> has published a very interesting piece of work on the influence of the method of coagulation. He worked on *Hevea* latex, dialysed until the original conductivity of  $3300 \times 10^{-6}$  was reduced to  $5 \times 10^{-6}$ .

He arrived at the following general conclusions: (1) Positive ions—as is the case with other negative colloids—produce coagulation. The most powerful action is exercised by strong acids and salt of di- and tri-valent metals. (2) Weak coagulants produce only flocculated or coalesced structureless masses, strong coagulants, clots having a reticular structure. The size and nature of the “mesh” varies with the coagulant. (3) The physical characteristics of the rubbers obtained with different coagulants or methods vary profoundly according to the method. Broadly speaking, the more powerful the coagulant the greater the tensile strength (breaking strain) and the smaller the distensibility (elongation).

The figures obtained by Henri were as follow:—

<sup>1</sup> Cf. Spence, *Lectures*, p. 25, and Torrilhon, *loc. cit.*

<sup>2</sup> Schidrowitz and Kaye, *J.S.C.I.*, 1907, p. 1264.

<sup>3</sup> *Compt. rend.*, 1907, tome cxliv. pp. 431–433; and *J.S.C.I.*, 1907, p. 264.

EXPERIMENTS ON *HEVEA* BY V. HENRI

Method of Coagulation.		Breaking Strain of Rubber.	Elongation at Break.
Heat (80° C.).	.	grms. 150	8.5
" (25° C.).	:	190	7.2
Acetic acid (weak)	.	175	7.5
" (strong).	:	210	7.1
Tri-chlor-acetic acid	.	325 <sup>1</sup>	6.8
Acid + Electrolyte 1	:	310	6.8
" + " 2	:	380	6.8
" + " 3	:	660 <sup>1</sup>	6.5

An interesting point in connexion with Henri's work is that under certain conditions *dialysed Hevea latex* is coagulable by heat, whereas ordinary latex of this species is not.

*Influence of the Method of Coagulation on Funtumia elastica.*—The following results (see next page) were obtained in my laboratory.<sup>2</sup>

It will be observed in the table that samples Nos. 3, 5, 8 and 10 are absent. These were samples which were not fully examined, but a few details concerning them may be given. No. 3 was a sample to which 5 per cent. of solid, powdered calcium chloride was added. After standing for about a month, the latex appeared quite unaltered. It was coagulated by means of heat. The rubber after pressing, but when still moist, showed a breaking strain of 180. After further drying, the sample showed an elongation of about 4.5, and a breaking strain of nearly 500, and a resiliency, at a strain of 450, of over 70 per cent. No. 8 was treated with an excess of solid magnesium sulphate. No coagulation took place, even after a number of days. No. 10 was treated

<sup>1</sup> It must not be assumed that the methods which give the highest results for breaking strain will produce the best commercial article. While strong coagulants produce a very close mesh structure—and therefore great mechanical strength—the rubbers obtained, particularly if an excess of the coagulant is employed, show a tendency to become hard and brittle.

<sup>2</sup> Schidrowitz and Kaye, *I.R.J.*, 1907, vol. xxxiv. p. 377.

## RUBBER

EXPERIMENTS ON *FUNTUMMA ELASTICA* LATEX BY SCHIDROWITZ AND KAYE

No. 1.	No. 2.	No. 4.	No. 6.	No. 7.	No. 9.	No. 11.	No. X.
Heated to 75° C., warmed with fresh quantities of water (at 50-60° C.) several times until wash water colorless. Then pressed and dried in a vacuum (at 40° C.).	Boiled for five minutes. Pressed lightly and boiled up with more water. Pressed again. Finally dried in a vacuum (at 40° C.).	Treated with ammonium oxalate and calcium chloride.	Precipitated with acetone; 3. Pressed and dried as others.	Creamed with water 1:5; and dried.	Diluted with CaCl <sub>2</sub> (to per cent after 1 week); 5. Then added a little ammonium oxide and heated to 100° F. Pressed, etc.	Boiled. Then boiled coagulum with more H <sub>2</sub> O. Pressed and then treated with resin solvent. Pressed and dried in a vacuum.	Boiled. Then precipitated from latex exactly neutralizing with alkali.
Yield of rubber from latex calculated to dry resin-free article. Caoutchouc, i.e. soluble rubber free from H <sub>2</sub> O and resin.	Per cent. 47.0	Per cent. 47.0	Per cent. Not exactly determined, but not good.	Per cent. 46.0	Per cent. 51.0 (contains more ash than the other) 91.74	Per cent. 43.0	Per cent. About 40
Dirt and insoluble substances.	81.9	80.60	85.47	80.90	94.32	..	..
Moist tensile strength (breaking strain) in grams per square millimetre.	0.64	1.73	0.43	1.76	3.54	..	..
Dry tensile strength.	120	190	117	190	220	364	..
Moist elongation.	..	..	..	..	..	..	..
Dry elongation.	6.0	4.25	2.17	290	220	364	..
Resiliency (dry). Resiliency (moist). <sup>1</sup>	..	5.0	3.8	5.6	4	6.6	..
	66	5.0	5.5	6.4	4	6.6	4.8
		6.0 (quite dry)	80	94	54	100	..
		57					

<sup>1</sup> The "moist" tensile strengths were determined on the samples after partial but equal drying. Parts of the samples were then completely dried (until quite clear) in a vacuum at 40° C. The "dry" tests refer to the samples so treated. The "resiliency" was arrived at by expressing the original length of the strip tested as a percentage of the length of the strip after a period of twenty-four hours had elapsed after the test was made. A sample which returned to its *original* length after this period would therefore have a resiliency of 100.

with 5 volumes of a 5 per cent. ammonium oxalate solution. No coagulation took place. Analyses of five samples from bulk, made experimentally from the same batch of fresh latex by the Mabira Forest Co. in Uganda by different methods, disclosed considerable variation, particularly in regard to nitrogen content and viscosity, the former varying between 0.25 per cent. and 0.46 per cent., the latter between 11,400 and 18,500.

Quite recently Frank and Marckwald have published a series of interesting papers dealing with the properties of *Manihot Glaz.*<sup>1</sup> and *Funtumia elastica*<sup>2</sup> rubbers prepared by different methods and in different districts.

<sup>1</sup> *G.Z.*, 1911, vol. xxv. p. 193.

<sup>2</sup> *Ibid.*, p. 877.

## CHAPTER IX

### CRUDE RUBBERS COMPARED—"TACKINESS"

FROM the foregoing chapters it will have been gathered that commercial crude rubber is by no means a homogeneous product, and that its chemical composition and physical properties depend principally (*a*) on the quality of the latex, (*b*) on the method of coagulation and curing. From an industrial or commercial point of view, the value of a rubber depends on (*a*) the percentage of pure rubber, (*b*) the nature of the non-rubber, (*c*) the physical condition of the material. These three factors jointly determine the most important attribute of a commercial rubber, namely, its vulcanizing capacity.

As far as the amount of the various *groups* of secondary substances (resin, etc.) are concerned, there is very little difference between well prepared high class rubbers derived from different latices, but this does not apply to low grade rubbers. Between these two extreme groups may be placed grades such as the medium African and South American varieties. Such rubbers are, as a rule, relatively poor merely on account of improper methods of preparation, and because they contain much water and dirt.

#### PHYSICAL CONDITION OF COMMERCIAL RUBBERS

While the chemical figures—particularly for rubbers of the same species—may differ only slightly for different

specimens, the viscosity numbers are subject to wide variations. Viscosity is a measure of molecular complexity and of physical aggregation. The *a priori* assumption that there must, therefore, be some relationship between the viscosity and strength or "nerve," is justified, and has, as a matter of fact, been confirmed by published experimental work.<sup>1</sup> There are only two methods known which can be generally employed for the purpose of determining the physical condition of a rubber, namely, vulcanization and viscosity measurements, but whereas vulcanization tests, in order to be of real utility, require considerable time and a very great experience, viscosity may be determined rapidly and in a very simple manner. As an indication of the practical utility of the viscosity method, I may point out that whereas it is impossible to judge the relative value—as far as strength or "nerve" are concerned—of different plantation crêpes by the hand-pulling test or by appearance, the viscosity test is an excellent guide in this connexion.

Broadly speaking, one may say that the physical properties of a commercial rubber determine or rather connote the specific quality of the rubber substance as such, the chemical constituents its commercial value subject to the qualifying factor of the physical properties. To take two examples—both corresponding, I may add, to cases that have occurred in my practical work:—(1) Two rubbers (*A* and *B*) contain approximately equal quantities of rubber, resin, ash, moisture, etc., and are similar in colour and general appearance. *A* is firm, nervous, shows a high viscosity figure and vulcanizes well, but *B* is tacky or "pasty," shows a low viscosity and gives poor results in manufacture. The value of *A* may be as much as three or four times that of *B*. (2) *A* and *B* are both good strong rubbers, similar in colour and general appearance. Both give high viscosity figures and vulcanize well. *A* contains, say, 2 per cent. more resin; 1 per cent. more ash; 3 per cent.

more insoluble matter, and 4 per cent. more moisture and other non-rubber constituents than *B*. It contains, therefore, 10 per cent. less rubber substance, and the difference in value will (or should) be about 10 per cent. plus some slight extra allowance for variability in vulcanization, washing, etc. I assume that in both cases *A* and *B* are of the same species. When we come to deal with low grade material, valuation is an exceedingly difficult problem. To take an example: Jelutong containing, say, 48 per cent. of solids, of which nearly 10 per cent. is rubber, the balance substantially resin, has, during the past few years (I exclude the abnormal prices obtaining during the "boom" of 1910), sold normally at 2d. to 2½d. per lb. Accra paste and Niger flake, containing roughly 80 per cent. of solids, including 8 to 10 per cent. of rubber, the balance substantially resin, have been selling at about 1s. to 1s. 3d. The lower price fetched by the Jelutong is obviously not due to the quality of the rubber in the material, as this is of a very high grade, and, moreover, Jelutong as such behaves very well in mixings. We must then assume that either the resin in the African low grades has some special virtue, or that the material as a whole has some specific sphere of utility. A more probable explanation is that many manufacturers have used these low grade "Africans" for a long time in standard mixings for special purposes, and do not care to depart from established practice. The limited supply of these "Africans" compared with that of Jelutong will therefore explain the difference in price.

#### "TACKINESS"

Perhaps the most interesting manifestation of abnormal physical condition in a rubber is that known as "tackiness." Many theories have been elaborated regarding the cause of tackiness, but, interesting as are the observations of a number of workers in this direction, there has been a tendency—which, as I have pointed out elsewhere (see p. 116),

has been frequently and sometimes disastrously evident in other branches of rubber science and technology—to apply to rubber generally the experience gained in connexion with a specific variety. One fact appears, however, to have now been established on a firm basis of experimental proof, and this is, that tacky rubbers always show a low state of colloidal aggregation or of molecular complexity compared with sound rubbers of the same species. I have always found the viscosity of tacky rubbers to be very low,<sup>1</sup> and in no case have I found that the decreased viscosity is directly referable to the presence of the ordinary non-rubber constituents (resin, proteids, etc.) in abnormal quantity. Spence<sup>1</sup> has shown that a sound and a tacky sample respectively of *Funtumia elastica* exhibited no material difference in regard to carbon and hydrogen content (elementary analysis), and that they gave substantially the same figures on bromination. The phenomenon of tackiness is certainly not—as was at one time believed—due to oxidation or chemical change, and may be safely regarded as a physical degradation of the rubber substances. Among the causes of tackiness, sunlight, heat, bacteria, enzymes, faulty coagulation, small quantities of specific chemical substances, absence of moisture and the presence of excessive moisture, have been observed or suggested.

*Sunlight*.—Certain rubbers—for instance, Guayule—are very susceptible to sunlight, a very short exposure sufficing to bring about an ultimate profound change. Brindejong<sup>2</sup> and Bertrand<sup>3</sup> have made interesting observations in this connexion, but the latter agrees that other factors, such as the method of coagulation, may play an important part in producing tackiness. Within my own experience, a certain rubber prepared by a method which I will call *A* always became tacky after a brief period. The same rubber prepared by a method *B* did not become tacky even after exposure to sunlight and diffused light for several months

<sup>1</sup> Cf. Spence, *I.R.J.*, Quarter-Century Number, pp. 44 *et seq.*

<sup>2</sup> *G.Z.*, 1908, vol. xxiii. p. 213.

<sup>3</sup> *Lectures*, p. 200.

*Heat* is undoubtedly an important factor in producing tackiness. Rubbers vary considerably in regard to the degree of heat which will cause physical deterioration, but it is probable that overheating due to improper stowage on ship-board or elsewhere has produced more tackiness than any other cause. Excessive heat during the drying period is also the cause of much tackiness.

*Bacteria*.—Bertrand (*loc. cit.*) has argued that, as sunlight, which is well known to be inimical to bacterial life, is known to cause tackiness, it is not likely that bacteria are responsible for that condition. Moreover (and this I am able to confirm from my own observations), the use of antiseptics by no means always prevents tackiness. However, as Spence<sup>1</sup> points out, it is possible that bacteria may be responsible for producing a condition in rubber favourable to the development of tackiness, and from the practical experience I have in this connexion, I agree that there is much to support this view.

*Enzymes*.—Bamber<sup>2</sup> is of opinion that enzymes play an important part in producing tackiness, but Spence has pointed out that tackiness has been produced in rubber with which the greatest trouble has been taken to ensure the complete removal of protein and enzymes. It does not, however, follow that in other cases enzymes may not either cause, or produce, a condition predisposing rubber to tackiness. According to a private communication to me by Mr. G. A. Morton, he has isolated an enzyme which will produce tackiness in any rubber, including fine hard Para.

*Coagulation*.—Starting from the assumption that certainly the state of colloidal aggregation and perhaps the complexity of the rubber molecule are mainly or largely dependent on the method of coagulation, and that tackiness is simply the outward manifestation of colloidal degradation or depolymerization, it is obvious that the method of coagulation is of vital importance in regard to the tackiness

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Lectures*, p. 201.

problem. Bertrand<sup>1</sup> has made interesting observations in this connexion, and experiments of my own connected with the coagulation of a certain latex in bulk have clearly demonstrated the connexion between (*a*) method of coagulation, (*b*) physical aggregation (as measured by viscosity), and (*c*) disposition to tackiness.

*Specific Chemical Substances.*—Spence (*loc. cit.*) has published details of an experiment indicating that a very small quantity of sulphuric acid may produce tackiness in *F. elastica*. On the other hand, Frank and Marckwald<sup>2</sup> point out that they have examined *F. elastica* rubber coagulated with sulphuric acid, and also with hydrofluoric acid, which was of excellent quality, and showed no sign of tackiness. While mineral acids may in some cases be productive of tackiness, we know that strong organic acids (*e.g.* acetic acid, trichloracetic acid, etc.) have a tendency (especially if used in excess) to produce hard and brittle, but not soft or tacky rubbers. Alkalies, undoubtedly, have in many cases a tendency to produce tackiness.<sup>3</sup> Speaking broadly, our knowledge of the mechanism of coagulation distinctly suggests that alkalies are likely to promote, acids to prevent, tackiness, at any rate within certain limits.

I have dealt with the subject of "tackiness" in some detail, as it is of great industrial importance. On the basis of a very considerable practical experience I venture to sum up the essential points to be kept in mind by the crude rubber producer as follows:—

1. The method of coagulation should be selected with a view to the production of rubber in the highest possible form of physical aggregation, but this is subject to the consideration that the "strong" coagulants (*i.e.* coagulants such as trichloracetic acid or acetic acid), particularly if

<sup>1</sup> Bertrand, *Le Caoutchouc et la Gutta-percha*, 1908, vol. v. 1941.

<sup>2</sup> Z.K., 1909, 5, p. 189.

<sup>3</sup> Cf. Fox, *I.R.J.*, 1911, vol. i. p. 28. I am able to confirm Fox's views from my own experience of large scale work.

used in excess, produce rubbers of so firm and intricate a network structure that they become brittle very rapidly.

2. Antiseptic treatment is always desirable, if not always necessary. Cleanliness is always essential.

3. Overheating in drying-rooms and ship-holds must be carefully guarded against, and sunlight avoided.

## CHAPTER X

### THE CHEMISTRY OF CRUDE RUBBER

THE chemistry of crude rubber falls naturally into two subdivisions—(a) The chemistry of the pure hydrocarbon; (b) the chemistry of the secondary constituents. It is, I think, more convenient to consider the latter first.

#### RUBBER RESINS

The term resin is applied generally to the substances which may be extracted from crude rubber, by means of acetone or alcohol.<sup>1</sup> So far, comparatively little pure chemical research has been done on these bodies, but the results obtained indicate that the "resins" consist of substances containing oxygen in varying quantities. According to Tschirsch,<sup>2</sup> the carbon and hydrogen in the resins frequently stand in the same relation to one another as in rubber, which would indicate that they are oxidation products. This, in view of the recent work of Hinrichsen and Marcusson (see p. 141), does not appear to be at all likely as a general rule. The resin from certain very resinous latices (such as that obtainable from *Dyera* varieties) contains a body which is probably a compound of a vegetable cholesterol with cinnamic acid. Harries<sup>3</sup> has

<sup>1</sup> Some rubbers contain resins which are very insoluble in the ordinary solvents. As a rule, they may be removed by extraction with glacial acetic acid.

<sup>2</sup> *Die Harze*, 1906, vol. i. pp. 989 *et seq.* (Leipzig, Bornträger).

<sup>3</sup> *G.Z.*, 1910, vol. xxiv. p. 850.

recently stated that a characteristic property of rubber resins generally is that they form ozonides which are very insoluble in chloroform and in carbon-tetra-chloride. Broadly speaking, there are two classes of rubber resins, namely, soft and hard resins. Thus Jelutong contains a white crystalline *hard* resin, soluble with difficulty in cold, but readily in hot absolute alcohol; and a soft yellowish resin, very readily soluble in cold alcohol. Technically, hard resins are preferable to soft; indeed, a resin content up to 8 per cent. is not a serious matter provided the bulk of it is of the hard variety.<sup>1</sup> Similarly in gutta-percha there are, according to Tschirsch,<sup>2</sup> a hard, white, relatively insoluble resin belonging to the "Albane" class, of the composition  $(C_{20}H_{32}O)_2$ , and a soft, more soluble resin belonging to the "Fluavil" class, which is represented by the formula  $(C_{10}H_{16}O)_2$  or  $(C_{10}H_{16}O)_4$ .

According to Ditmar,<sup>3</sup> the resin from Congo rubber melts at  $74^{\circ}.0$  C. and is absolutely unsaponifiable. On the other hand, resin from Borneo rubber gives a saponification number of 28.1 and melts at  $92^{\circ}.5$  C. It contains no free acid. From a Madagascar rubber he obtained a resin melting at  $102^{\circ}.0$ . A. Wagner<sup>4</sup> examined the behaviour of a number of resins towards solvents. The following figures were obtained in my laboratory<sup>5</sup> with different rubbers:—

The figures indicate c.c.  $\frac{N}{10}$  alkali absorbed by 1 grm. of the resin.

	Sample 1.	Sample 2.	Sample 3.
<i>Funtumia elastica</i> resin . . .	8.83	6.70	...
<i>Castilloa elastica</i> resin . . .	16.61	...	...
Plantation Para (Ceylon) resin .	6.03	27.03	30.2

<sup>1</sup> Thus properly prepared *Funtumia elastica* contains substantially only hard resins, and may, from the manufacturing point of view, be regarded as a first-class article even with as much as 8 per cent. of resin.

<sup>2</sup> *Op. cit.*, p. 907.

<sup>3</sup> *G.Z.*, 1907, vol. xxi. pp. 666 *et seq.*

<sup>4</sup> *Ibid.*, p. 498.

<sup>5</sup> Schidrowitz and Kaye, *J.S.C.I.*, 1907, p. 132.

Sample No. 1.—Plantation Para contained much insoluble matter, obviously due to oxidation, the other samples relatively little. It is remarkable, therefore, that it absorbed much less alkali than the other samples.

Recently Hinrichsen and Marcusson<sup>1</sup> have carried out some interesting work on the optical properties of rubber resins, and found that all the rubbers examined, excepting *Hevea* specimens, contain markedly active resins.

The active resins examined were all dextro-rotatory, varying from roughly  $[\alpha] D + 12$  for Upper Congo and Guayule to  $[\alpha] D + 50.9$  for Jelutong. They also found that the saponification numbers of the resins examined varied considerably, the general rule obtaining that the more active the resin the less saponifiable matter it contains. Thus Para resin (non-active) contained 15 per cent. of unsaponifiable matter, *Funtumia elastica* ( $[\alpha] D + 32.9$ ) 74 per cent., Jelutong 100 per cent. The unsaponifiable matter was more active than the saponifiable—for instance as  $[\alpha] D + 24.5 : [\alpha] D + 13.0$  in the case of Upper Congo. Hinrichsen and Marcusson also investigated the iodine absorption (Hübl) of the resins, and obtained numbers varying from 30.6 for Jelutong to 118 for Para. The authors referred to are of opinion that the active rubber resins are not oxidation or other rubber derivatives. They deresinified a sample of *Funtumia*, and subsequently exposed the sample in such a way that oxidation and tackiness were brought about. On again deresinifying, they obtained 3.11 per cent. of an *inactive* resin. They consider this proof of the general hypothesis that as rubber as such is inactive, its oxygen and other derivatives must also be inactive, and that the active resins are not rubber derivatives.

#### NITROGEN IN RUBBER

All crude rubbers contain varying amounts of nitrogen. In general analytical work it is still usual to return the

<sup>1</sup> Z.K. angew. Chem., 23, 1910, p. 49.

whole of this element as "proteid," but there is not the slightest doubt that this is incorrect, for it has been shown on several occasions that a part of the nitrogen may be present in other forms. Thus it has been shown<sup>1</sup> that whereas a sample of crude *Castilloa* yielded a total of 2.10 per cent. of soluble nitrogen (calculated as proteid), only 1.66 per cent. (roughly three-quarters) of this could be regarded as true proteid matter. Similar observations have also been made in connexion with the examination of various latices.<sup>2</sup> It is possible that these facts account for the apparent anomaly that whereas in some rubbers a high percentage of nitrogen appears to connote undesirable qualities—particularly in regard to stability and vulcanizing capacity—in others this is not the case, or, at any rate, not to anything like the same extent.

### INSOLUBLE MATTER

There is in all commercial rubbers a certain proportion of a substance (or substances) insoluble in ordinary rubber solvents such as benzene, chloroform, or carbon-bisulphide. It was formerly believed<sup>3</sup> that rubber consisted of two isomeric substances, the one constituting the "nervous" the other the "adhesive" principle, and, moreover, it was held that the "insoluble matter" and the "nervous principle" were identical. Weber exploded this theory by showing that in fine Para (which contains a relatively high amount of insoluble matter) the average quantity of this material amounted to no more than 3.5 per cent., and that it is not a hydrocarbon at all. He (Weber) regarded the insoluble constituent of fine Para as a body of the formula  $C_{30}H_{68}O_{10} = 3(C_{10}H_{16}) + 10H_2O$ , a link between rubber and the "complex carbohydrates, the celluloses in particular." Curiously enough,

<sup>1</sup> Schidrowitz and Kaye, *J.S.C.I.*, 1907, p. 130.

<sup>2</sup> Cf. Spence, *Q.J. Inst. Comm. Research*, Reprint No. 9, p. 12, and Fickendey, *loc. cit.*, p. 122.

<sup>3</sup> Weber, *Chemistry of India-Rubber*, pp. 62 *et seq.*

Weber omitted to examine the insoluble matter for nitrogen. Spence<sup>1</sup> re-investigated the whole question, and found that the insoluble matter in fine Para consists very largely of proteid matter, the highest nitrogen content observed being 5.4 per cent., corresponding to 33 per cent. of proteid.<sup>2</sup> The insoluble constituent in fine Para forms a fine network throughout the mass through which the solvent must work its way before solution of the rubber substance can be brought about. This accounts for the fact that fine Para which has not been masticated—the process of mastication breaks up the network of fibrous proteid, etc.—dissolves very slowly. It must not be assumed that the insoluble matter in commercial rubbers consists always or mainly of nitrogenous matter. On exposure to the atmosphere, the rubber substance gradually becomes (I exclude "tacky" rubber) hard and brittle, and extremely insoluble. Some plantation rubbers in the form of thin sheets and crêpe exhibit this phenomenon to a marked degree. There is reason to believe that in such cases the action of the atmosphere is not alone to blame, but that the use of an excess of acetic acid in coagulation is a contributory factor. On the other hand, clean, fresh plantation rubbers contain practically no insoluble matter of any kind. The nature of the insoluble substance in some plantation rubbers still awaits investigation. If it is an oxidation product it is apparently not identical with "Spiller's resin,"<sup>3</sup> a shellac-like body *soluble in alcohol* of the composition  $C_{30}H_{48}O_{10}$  which forms on prolonged exposure of rubber to the atmosphere. In connexion with the nature of the insoluble matter in various rubbers, it is interesting to note that *F. elastica*,<sup>4</sup> although a highly viscous rubber, generally dissolves very readily. This appears to confirm Fickendey's view (*loc. cit.*) that *F. elastica* latex contains no true proteid: at

<sup>1</sup> *Q.J. Reprint*, No. 13, and *J.S.C.I.*, 1907, p. 1287.

<sup>2</sup> Spence considers it likely that the nitrogen is present as a glyco-protein, in which case 60 to 70 per cent. of the "insoluble" constituent might consist of proteid matter.

<sup>3</sup> *Journ. Ch. Soc.*, 1865, p. 44.

<sup>4</sup> Coagulated by heat.

any rate, if proteid is present it is not in the form of a reticulated fibroid network as is the case in fine Para. (*Regarding the nature of the mineral matter, sugars, etc., that may be present in crude rubber, see chapter on "Rubber Latices and Coagulation."*)

### COMPOSITION AND CONSTITUTION OF THE RUBBER MOLECULE

*Composition.*—The earlier work<sup>1</sup> on the composition of the rubber molecule tended to show that the more highly crude rubber is purified the nearer it approaches to the formula  $(C_{10}H_{16})_n$ . In view of the later work on rubber derivatives, fission products and syntheses of the material, this formula may now be taken as definitely established.

*Constitution.*—Modern views on the constitution of the rubber molecule are mainly based (1) on the syntheses of rubber and isoprene (a product obtained from rubber by dry distillation) by Tilden, Bouchardat, Euler, Harries, etc.; and (2) on the study of rubber derivatives chiefly by Harries. The work on the dry distillation of rubber by Himly,<sup>2</sup> Greville Williams,<sup>3</sup> and Bouchardat,<sup>4</sup> and later by Weber and others, may be regarded as the foundation of the structure of modern rubber chemistry. Among the numerous isomeric hydrocarbons of the formula  $C_5H_8$  isolated from the products of dry distillation, two are of especial interest, namely, *Dipentene* or *Caoutchoucene* (Himly, B.P. 171°) and *Isoprene* (Greville Williams, B.P. 37° to 38°). Dipentene was studied more particularly by Ipatiew,<sup>5</sup> and he came to

<sup>1</sup> Cf. Weber, *The Chemistry of India-Rubber*, pp. 5 *et seq.* In view of the exhaustive discussions of this subject in the works of Weber, Ditmar, and others, and that it is mainly of historical interest, I refrain from entering into details.

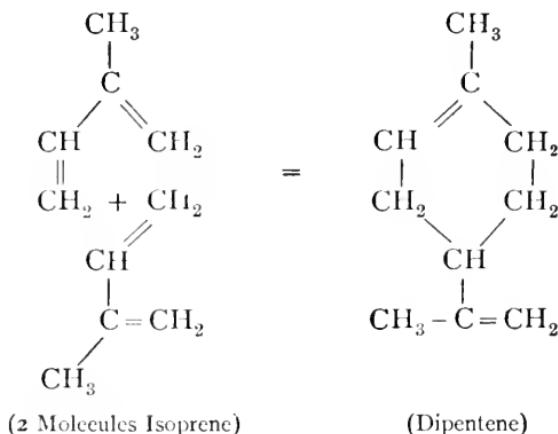
<sup>2</sup> Liebig's *Annalen*, 1838, 27, p. 41.

<sup>3</sup> *Proc. Royal Soc.*, 1860, 10, p. 517.

<sup>4</sup> *Jahresber.*, 1875, pp. 389 and 1157.

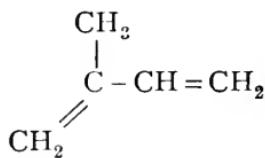
<sup>5</sup> *Journ. f. Prakt. Chem.*, 1879, 55, p. 11.

the conclusion that it was formed by the condensation of 2 molecules of isoprene in the following manner:—



This view was confirmed by Perkin,<sup>1</sup> who effected a synthesis from d-keto-hexahydro-benzoic-acid-ester.

*Isoprene.*—From the work of Mokiewsky<sup>2</sup> and of Ipatiew and Wittorf,<sup>3</sup> and finally as the result of the synthesis of this body from  $\beta$ . methyl-pyrollidine by Euler,<sup>4</sup> it is clear that isoprene is constitutionally  $\beta$ . methyl-divinyl of the formula—



To Bouchardat<sup>5</sup> must be given the credit of having effected what was probably the first synthesis of rubber, for he found that on heating isoprene with aqueous hydrochloric acid condensation or polymerization took place, and that small quantities of a material which—judged by solubility and dry distillation—appeared to be rubber, formed. The

<sup>1</sup> Proc. Chem. Soc., 1904, 20, p. 86.

<sup>2</sup> *J. Russ. Phys.-Chem. Soc.*, 27, p. 516.

<sup>8</sup> *J. f. Prakt. Chem.*, 1897, 55, p. 2.

<sup>6</sup> *Compt. rend.*, 1875, 80, p. 1446; and 1879, 89, p. 1117.

<sup>4</sup> *Ibid.*, 1898, 57, p. 131.

next link was supplied by Tilden,<sup>1</sup> who, working on isoprene obtained by him by passing turpentine vapours through hot tubes, obtained a substance, which was undoubtedly rubber, by two distinct methods—(a) By means of hydrochloric acid (thus confirming Bouchardat) and (b) by spontaneous polymerization. By method (a) the yield was small; method (b) gave a good yield but occupied several years. As it has been repeatedly suggested that Tilden gave no proof that the substance obtained by him was actually rubber, it is of interest to quote his own words:<sup>2</sup>—

“Specimens of isoprene were made from several terpenes in the course of my work on these compounds, and some of them I have preserved. I was surprised a few weeks ago<sup>3</sup> at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In the place of a limpid colourless liquid the bottle contained a dense syrup in which was floating several large masses of a solid of a yellowish colour. Upon examination this turned out to be india-rubber. . . . The artificial india-rubber, like natural rubber, appears to consist of two substances, one of which is more soluble in benzene or carbon bisulphide than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characters with a similar preparation from Para rubber. The artificial rubber united with sulphur in the same way as ordinary rubber, forming a tough elastic compound. . . .”

I may add that a sample of this rubber was on view at a recent exhibition in London.

The synthesis of rubber from isoprene had, however, thrown no definite light on its constitution, and it is to the work of Harries<sup>4</sup> that we owe our first definite information on this subject. He observed that ozone reacts with rubber,

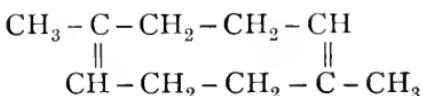
<sup>1</sup> *Chem. News*, 1882, 45, p. 120; and *Trans. Birmingham Phil. Soc.*, 1892.

<sup>2</sup> *I.R.J.*, 1908, vol. xxxvi. pp. 321 *et seq.*

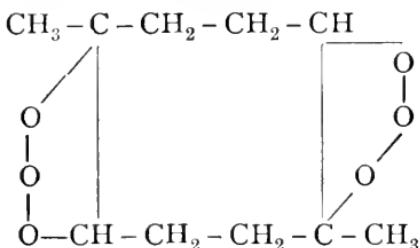
<sup>3</sup> This refers to 1892 (cf. footnote).

<sup>4</sup> *B.*, 1904, 37, p. 2708, and *ibid.*, 1905, 38, p. 1195.

forming a compound  $C_{10}H_{16}O_6$ . As ozone was known to form additive compounds with bodies containing double linkages, he concluded that the rubber molecule contains two double bonds. On hydrolyzing the rubber ozonides, lævulinic aldehyde and lævulinic acid were formed as the end products of the reaction. This led Harries to assume that rubber is an eight-ring derivative, namely, 1,5 dimethylcyclo-octadien.



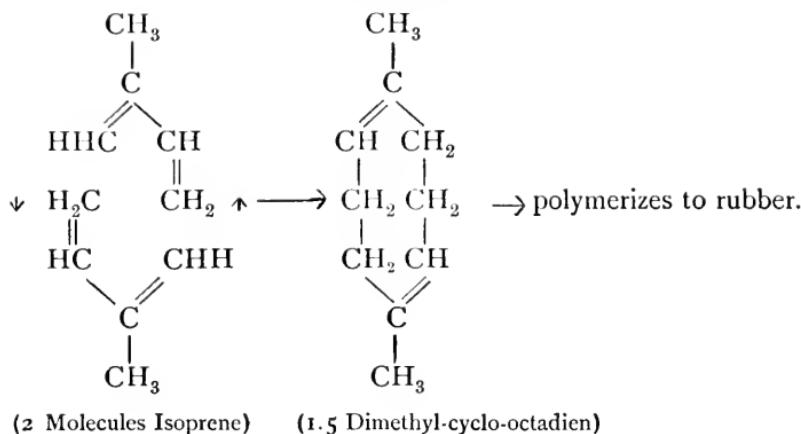
The corresponding ozonide would possess the formula—



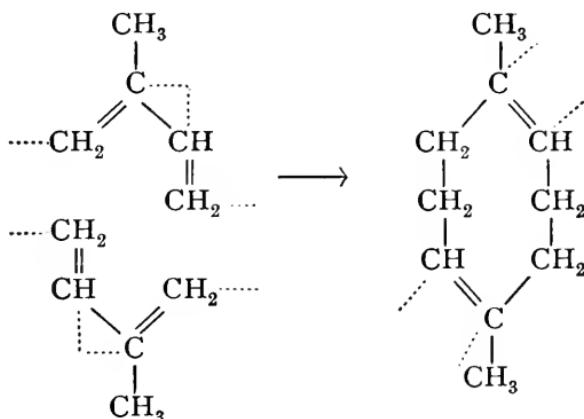
As a result of this work Harries and his school were inclined to doubt the correctness of the assertions that rubber had actually been synthesized from isoprene, inasmuch as this would involve the assumption of a somewhat abnormal intramolecular re-arrangement of linkages. At a later date, however, Harries<sup>1</sup> himself synthesized rubber from isoprene—by heating in tubes with glacial acetic acid and acetic anhydride<sup>2</sup>—and came to the conclusion that the condensation and subsequent polymerization could be explained with the aid of the theory of conjugated linkages as follows:—

<sup>1</sup> *G.Z.*, 1910, vol. xxiv. p. 854.

<sup>2</sup> He observed that if rubber is boiled with these reagents, it tends to "depolymerize." It occurred to him that the reaction might be reversible, and this led him to study the action of acetic anhydride and glacial acid on isoprene.



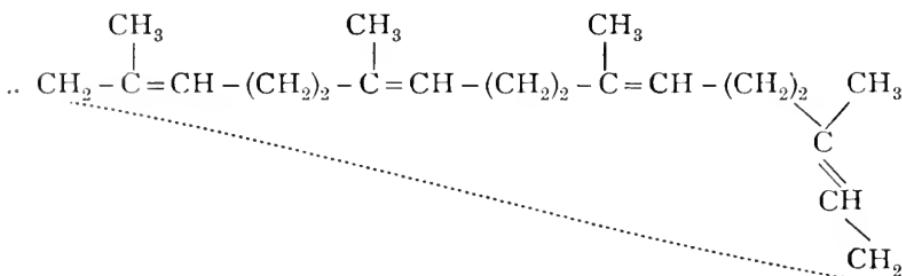
The condensation takes place at the carbon atoms in the 1,4 position, as is the case with all additive reactions in bodies possessing conjugated double linkages. Professor J. T. Hewitt has suggested to me that the mechanism of the condensation may be more readily explained according to Thiele's theory of partial valencies as follows:—



I have already referred to the fact that on hydrolyzing rubber ozonides, laevulinic acid and laevulinic aldehyde are obtained, but in the course of further work Harries<sup>1</sup> found that whereas, in the case of Para rubber laevulinic aldehyde is the predominant product of hydrolysis, the reverse is the

<sup>1</sup> *B.*, 1905, 38, p. 3985, and *G.Z.*, vol. xxii. p. 305.

case with the ozonides derived from gutta-percha and from certain African rubbers—*i.e.* lävulinic acid is the main product obtained. Harries from this argues that the hydrocarbon in Para, and in gutta and certain African varieties respectively, are differently constituted. The rubber hydrocarbon contains no asymmetrical carbon, but the facts may be explained by assuming that the ozonide group occupies a different position relatively to the plane of the eight-ring in space—a *cis*-position in the one, a *trans*-position in the other case. Pickles<sup>1</sup> suggests that rubber does not (as Harries' theory demands) consist of a number of rings polymerized to a complex molecule, but of a single ring consisting of a number of unsaturated  $C_5H_8$  nuclei united in the following fashion:—



and that the number of  $C_5H_8$  complexes may vary in different kinds of rubber, the difference in properties being probably due to this variation in the number of complexes contained. He considers that rubber contains at least eight  $C_5H_8$  complexes. According to Pickles, the known facts are better explained by his hypothesis than by Harries' formula.

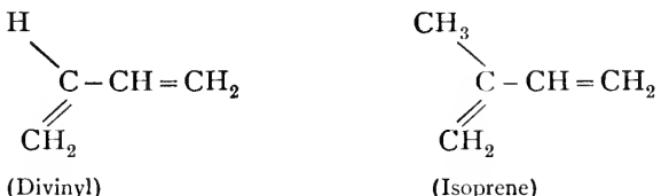
### COMMERCIAL SYNTHETIC RUBBER

The manufacture of synthetic rubber on a commercial scale will only be possible if a suitable low-priced raw material, capable of transformation at a low cost and with

<sup>1</sup> *J. Ch. Soc.*, 1910, pp. 1085 *et seq.*

a high yield, can be found. So far these conditions do not appear to have been fulfilled. Put briefly, no synthetic process which cannot produce rubber to sell at a profit at about 1s. 3d. to 1s. 6d. is likely to be of enduring value. Considerable activity is, however, being displayed in this direction, and recent patent literature throws an interesting light on the lines along which the work is being carried on.

The Farbensfabriken vormals F. Bayer & Co.<sup>1</sup> have taken out a patent for a process producing a substance "similar in its properties to natural caoutchouc," which consists in heating erythrene (divinyl) with or without polymerizing agents. I may point out that the relationship of isoprene to divinyl is—



The condensation product is probably, therefore, a lower homologue of ordinary rubber.

The Badische Anilin und Soda Fabrik<sup>2</sup> have taken out a patent for producing a product possessing the properties of natural rubber by heating isoprene as such or with neutral or alkaline substances.

The same firm<sup>3</sup> have taken out a patent for "substances possessing all the properties of natural caoutchouc," the process consisting in the heating of  $\beta$ - $\gamma$ -dimethyl  $\alpha$ - $\gamma$ -butadiene (methyl-isoprene?) with or without various polymerizing agents. In connexion with this process—which apparently produces a higher homologue of rubber—it is interesting to note that a process for the production of the dimethyl-butadiene by heating pinacone and pinacoline (*acetone* derivatives) with catalytic dehydrating reagents such as alumina, has also been patented by the said firm.

<sup>1</sup> *I.R.J.*, 1910, vol. xl. p. 510.

<sup>2</sup> *G.Z.*, 1911, vol. xxv. p. 593.

<sup>3</sup> *J.S.C.I.*, 1911, p. 38.

It is obvious, therefore, that processes for the production of rubber and of the analogous higher and lower homologues are being developed step by step, but I am not aware of anything indicating that such processes can as yet compete commercially with the natural product at the lowest prices at which the latter can be produced.

### DERIVATIVES OF THE RUBBER HYDROCARBON

In addition to the *oxygen* derivatives and ozonides already referred to, it is of interest to note that Herbst<sup>1</sup> obtained, by passing a current of air for a prolonged period through a warm benzine solution, two bodies  $C_{10}H_{16}O$  and  $C_{10}H_{16}O_3$ . The latter—which is insoluble in light petroleum—was found to correspond in its properties to Spiller's resin.<sup>2</sup> Gladstone and Hibbert<sup>3</sup> obtained by the action of *chlorine* on a chloroform solution a substance  $C_{10}H_{14}Cl_8$ , and Weber<sup>4</sup> prepared an iodide of a composition corresponding closely to  $C_{10}H_{16}I_3$  in a similar manner. It is, however, doubtful whether these derivatives—particularly the iodide—are homogeneous products. The *bromine* derivatives are of particular interest, inasmuch as analytical processes for the determination of rubber have been based upon them. Gladstone and Hibbert obtained an addition product  $C_{10}H_{16}Br_4$ , and a further body  $C_{10}H_{15}Br_5$ , in which one atom of hydrogen is replaced by bromine. The normal product of bromination is the tetrabromide, a fairly stable body which may be heated to nearly  $60^\circ$  for a short period (*e.g.* sufficient to dry the substance for analytical purposes) without undergoing material decomposition. It may be readily obtained, for instance, by allowing a solution of bromine (or iodo-bromine) in  $CHCl_3$  or  $CCl_4$  in slight excess to act on a solution of rubber in benzene or chloroform.

### THE NITROUS ACID AND NITRIC OXIDE derivatives,

<sup>1</sup> *B.*, 1906, 39, p. 523.

<sup>3</sup> *J. Ch. Soc.*, 1888, p. 682.

<sup>2</sup> Cf. p. 143.

<sup>4</sup> *Chemistry of India-Rubber*, p. 36.

which have formed the subject of much polemical discussion, are of considerable interest. The particulars regarding the main bodies obtained in this series are as follows:—

1. *Nitrosite* or *Nitrosate* ( $C_{40}H_{62}N_{10}O_{24}$ ), obtained by Harries<sup>1</sup> by the action of nitrous acid (obtained from nitric acid and arsenious acid) on crude rubber or a solution of rubber in light petroleum.

2. *Nitrosate* ( $C_{10}H_{12}N_2O_6$ ), obtained by Ditmar<sup>2</sup> by the action of nitric acid (concentrated) on crude rubber.

3. *Nitrosite* ( $C_{10}H_{16}N_2O_3$ ), obtained by Weber<sup>3</sup> by passing absolutely dry nitrous acid into a benzene solution.

4. *Nitrosate* ( $C_{10}H_{16}N_2O_4$ ), obtained by Weber by passing nitric oxide ( $N_2O_4$ ) into a benzene solution.

5. *Nitrosites b and c.* Harries<sup>4</sup> was able to obtain Weber's nitrosite (3), but found that if an excess of nitrous acid is employed, another body ( $C_{10}H_{15}N_3O_8$ )<sub>2</sub> called by him *Nitrosite b* is obtained. In the presence of moisture a different substance, which, according to Harries is ( $C_{10}H_{15}N_3O_7$ )<sub>2</sub>—termed by him *Nitrosite c*—is formed.<sup>5</sup>

*Sulphur derivatives.* See "Vulcanization," Chap. XI.

## PHYSICAL PROPERTIES OF CRUDE RUBBER

### Structure

Until comparatively recently,<sup>6</sup> it has been assumed that rubber substance is a structureless mass, but under "Coagulation" I have shown that this is not the case. Freshly coagulated rubber shows reticular structure, the "net" being composed of the original rubber globules. These globules, as I have indicated elsewhere, persist even after the rubber has been dried, and are visible in rubber solu-

<sup>1</sup> *B.*, 1901, 34, p. 2991.

<sup>2</sup> *Ibid.*, 1902, 35, p. 1401.

<sup>3</sup> *Ibid.*, 1902, 35, p. 1947.

<sup>4</sup> *Ibid.*, 1902, 35, p. 3256.

<sup>5</sup> Regarding the use of *nitrosites* for analytical purposes, see Chap. XV. p. 253. See also Caspary, *J.S.C.I.*, 1905, p. 1274.

<sup>6</sup> For literature see Schidrowitz, "The Structure of Crude Rubber," *J.S.C.I.*, 1909, p. 6.

tions made from dry rubber.<sup>1</sup> The "reticular" structure undergoes (see p. 126) a considerable change if the rubber is mechanically worked. In dry films prepared from a solution it is no longer visible, and this perhaps accounts for the fact that rubber obtained from a solution or that has been treated with rubber solvents is always of inferior quality so far as strength or "nerve" is concerned. I have observed, however, that if a film (obtained from a solution) is exposed to the action of diluted sulphur chloride (*i.e.* cold vulcanized), a pronounced network forms,<sup>2</sup> and I have very little doubt but that the increased mechanical strength imparted to rubber by vulcanization (hot or cold) is partly due to the emphasizing and development of the "net" structure of the crude material.

### *Specific Gravity*

According to Ditmar,<sup>3</sup> the specific gravity of pure rubber is 0.900, but in this regard the mechanical condition of the material is probably of importance. Pure commercial rubbers generally possess a specific gravity in the neighbourhood of 0.91. Thus for a series of plantation rubbers<sup>4</sup> values of from 0.9097 to 0.9261 were found. The latter figure was obtained on a badly "hardened" sample.

### *Thermal Properties*

The specific gravity of crude rubber gradually decreases on warming, and the material becomes soft and ultimately sticky. Like other highly complex organic substances, rubber possesses no definite melting point, and, as might be expected, the "melting points" of commercial varieties differ considerably. Ditmar<sup>5</sup> investigated this subject, and found that whereas fine Para melted at 188°, some inferior rubbers

<sup>1</sup> This observation of mine has been confirmed by Hinrichsen and Memmler, *op. cit.*, p. 42.

<sup>2</sup> See also Breuil, *Le Caoutchouc et la Gutta-percha*, 1905, pp. 3-6.

<sup>3</sup> *G.Z.*, 1907, vol. xxi. p. 670.

<sup>4</sup> Schidrowitz and Kaye, *J.S.C.I.*, February 28, 1907.

<sup>5</sup> *G.Z.*, 1907, vol. xxi. p. 669.

require a higher temperature. It is not clear whether there is any distinct connexion between melting point and vulcanizing capacity. If (crude) rubber is cooled, it commences to harden appreciably at about 50° F., until at about 35° to 40° F. it becomes quite hard and inelastic. If rubber is *stretched* and then warmed it contracts, and heat is absorbed. This has given rise to the erroneous notion that the effect of heat on rubber is normally the reverse of that of heat on other substances. At ordinary room temperatures crude rubber is adhesive, freshly cut surfaces readily joining up with slight pressure.

#### ACTION OF SOLVENTS

Water<sup>1</sup> is readily absorbed to a considerable extent by crude rubber, and the latter increases in volume. He found that as much as 18.7–26.4 per cent. of water (calculated to the weight of rubber) may be absorbed in a month, the volume of the rubber increasing by 15 to 16 per cent.

##### *Rubber Solvents*

Rubber forms typical colloidal solutions with petroleum and coal-tar hydrocarbons, carbon bisulphide, with many chlorine derivatives of methane, ethane, and ethylene, and with essential oils. Technically, the most important solvents are “solvent naphtha” (coal-tar and shale), and carbon bisulphide. For scientific work thiophene-free benzene or chloroform are most suitable, as they are readily obtainable in a pure state.

##### *Behaviour to Solvents*

When placed in a solvent, rubber gradually swells to a jelly, and finally—if sufficient solvent is employed—forms an extremely viscous colloidal solution. Weber and others have held that rubber does not form true solutions, and that it may be regarded as dissolving the solvent (forming a

<sup>1</sup> Payen, *Compt. rend.*, 1852, 34, 2.

colloidal sponge) rather than *vice versa*, but, according to more modern views, it is neither possible nor correct to draw any definite distinction between "colloidal" or ordinary solutions. Broadly speaking, a colloidal solution is one in which the specific surface of the particles is sufficiently great to produce the appearance of a non-homogeneous fluid when viewed in the ultra-microscope. When the particles are so small as to be invisible, they form with the solvent a "true" solution. Obviously this is a purely arbitrary distinction, which would vanish if more delicate optical measurements were possible.

The rate of solution varies widely according to the species and purity of the rubber,<sup>1</sup> and a very important factor in this connexion is the physical condition. Old (oxidised or otherwise hardened) rubbers are difficult to dissolve, and types such as fine Para, containing much proteid in a fibroid form (see p. 142), are—unless the fibrous structure is broken up mechanically—very slow in dissolving. Spence<sup>2</sup> states that heat does not hasten the rate of solution, but, viewed as a general statement, this is not in accord with my own experience.

*Mechanical working*—for instance, on the mixing rolls or in a masticator—greatly increases the solubility of rubber. This is partly due (in the case of a material such as fine Para) to the breaking up of the fibroid structure, partly to a direct effect on the state of aggregation of the rubber substance. This effect may be readily followed by viscosity measurements. I have been able by prolonged working on mixing rolls to reduce the viscosity in solution of fine Para to about one-twentieth of the original value. These facts have long been known in practice, and it is well known to manufacturers of rubber solution or "dough" for spreading, that when a solution of great mechanical strength and covering power is required, the less the material is "worked" the better. Up to a certain point, however, *adhesiveness* is increased by working. Weber and others have tried to

<sup>1</sup> Cf. Ditmar, *Die Analyse*, etc., p. 39.

<sup>2</sup> *Journ. Inst. Comm. Research in Tropics*, 1907, Reprint 10, p. 4.

explain the "tiring" of rubber by assuming that molecular depolymerization takes place, but there is nothing to indicate that this is the case, whereas the phenomenon is quite in accord with the well-known facts regarding other colloids, namely, that mechanical working may decrease the specific surface of the particles, and so the internal friction of a solution containing them. Until we are in a position to make reliable molecular weight determinations it will be impossible to pass a final judgment on this question.

### VISCOSITY OF RUBBER AND RUBBER SOLUTIONS

The extension—by applying a load—of a piece of solid rubber is in its general mechanical aspects very similar to the non-turbulent flow of a liquid through a narrow conductor. The effect of extension is attained mainly by overcoming the internal friction produced by the rubber molecules or aggregates passing one another. It is well known that the viscosity of a liquid, or of a solid contained in a liquid, connotes the state of aggregation, of molecular complexity or of physical aggregation, as the case may be. Considering these facts jointly, it appears more than probable that viscosity measurements of rubber solutions<sup>1</sup> must furnish valuable information regarding the physical or chemical state of aggregation of the rubber substance, and that the result of such measurements, made under proper conditions and correctly interpreted, must be intimately connected with the strength or "nerve" of the dissolved material. It does not, of course, necessarily follow that the viscosity figures will *directly* connote the most important—from a practical point of view—property of a rubber, namely, its vulcanizing capacity, but experience has shown that, with certain qualifications, this is the case, and that, in any case, the viscosity measurement is a far more accurate

<sup>1</sup> The application of purely mechanical (tensile) methods to crude rubber will be considered elsewhere (see Chap. XV. p. 253), but it may be desirable to state here that, for a number of reasons, the results obtained are not generally satisfactory.

test of the strength of a crude rubber than any purely mechanical tensile or "hand-pulling" method can possibly be. S. Axelrod,<sup>1</sup> with a view to examining the suitability and behaviour of various commercial washed rubbers from the point of view of the manufacture of technical "solution," examined the comparative rate of flow of a number of concentrated jellies through a separating funnel of special construction. The opening in the latter was so large, however, that for this and other reasons<sup>2</sup> and interesting as are Axelrod's results from many points of view, they cannot be regarded as actual viscosity measurements. Axelrod came to the conclusion that there was a distinct connexion between the rate of flow of the rubber jellies and the technical value of the rubbers as such. An important observation made by him was that the same relative order of "viscosity" is obtained with different solvents.

Until the preliminary investigation of this subject<sup>3</sup> was practically concluded, we had, owing to the fact that the title of his papers did not mention the word viscosity, and that it was nowhere indexed under that heading, no knowledge of Axelrod's work, but in any case, in view of the dissimilarity in objects and methods, no question of priority can well arise.

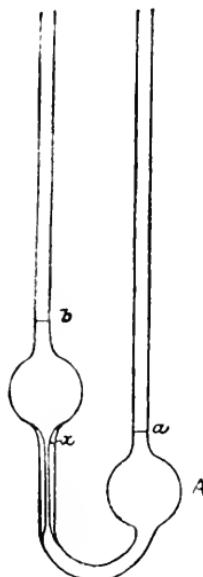


FIG. 3.—Viscometer  
(see p. 158)

*Dimensions.* — Total height, 24 cm.; capacity of *A*, 11 cc.; capacity of *B*, 10 cc.; length of capillary, 4.5 cm.; bore of capillary, 1 mm.

<sup>1</sup> *G.Z.*, 1905, vol. xix. p. 1053; vol. xx. p. 105.

<sup>2</sup> I refer to the use of impure solvents such as commercial light petroleum and "high boiling" benzene, to the "washed" (and therefore modified) condition of the rubbers, to the retention of all mechanical impurities, to the concentrated nature of the "solutions," to the, in many cases, indeterminate botanical nature of the crude rubbers, and to the attempt to compare the quality of the rubber on the basis of rate of flow at a fixed concentration.

<sup>3</sup> Schidrowitz and Goldsbrough, *J.S.C.I.*, 1909, p. 3. "The Viscosity of India-Rubber and India-Rubber Solutions: with special reference to its bearing on the strength or 'nerve' of Crude Rubbers."

For details of the methods employed by us, I must refer the reader to the publication mentioned below,<sup>1</sup> and it will

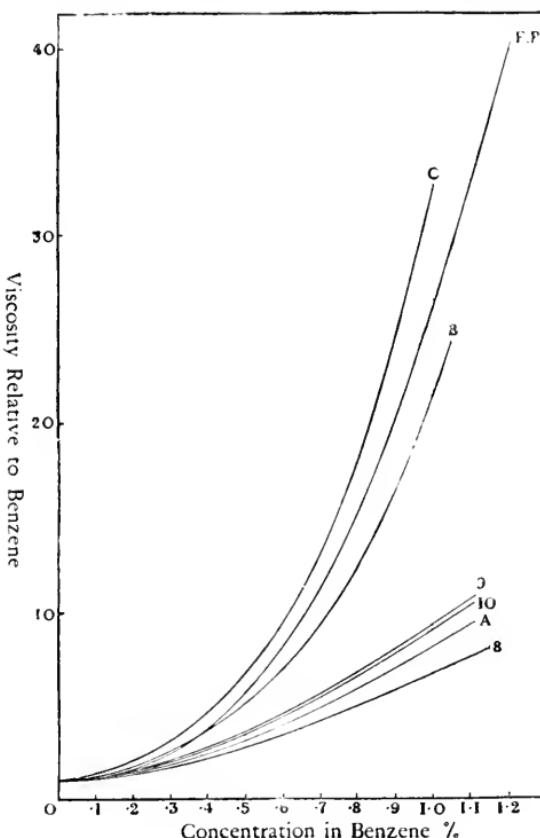


FIG. 4.—Viscosity Curves of Plantation Rubbers (see p. 163)

*Nature of Rubber* *Viscosity*

F.P. = Fine Para 1 year old and rather poor	.	.	.	7253
A = Plantation from 6 year old trees	.	.	.	1000
B = „ „ 13 „ „ } sheet	.	.	.	6653
C = „ „ 30 „ „ } sheet	.	.	.	8843
8 } Plantation crêpes from young trees }	.	.	.	1000
9 } (decidedly "short") }	.	.	.	1400
10 } (decidedly "short") }	.	.	.	1400

be sufficient to state here that we use (both for scientific and technical work) a viscometer of the Ostwald double bulb

<sup>1</sup> Schidrowitz and Goldsborough, *J.S.C.I.*, 1909, p. 3. "The Viscosity of India-Rubber and India-Rubber Solutions: with special reference to its bearing on the strength or 'nerve' of Crude Rubbers."

type (Fig. 3), dilute solutions (0.25 to 1.5 per cent.), dry thiophene-free benzene as solvent and a standard temperature of 20°. The solutions are filtered bright through glass wool, thus removing all mechanical impurities. Absolute measurements of the capillary, etc., are not necessary, the

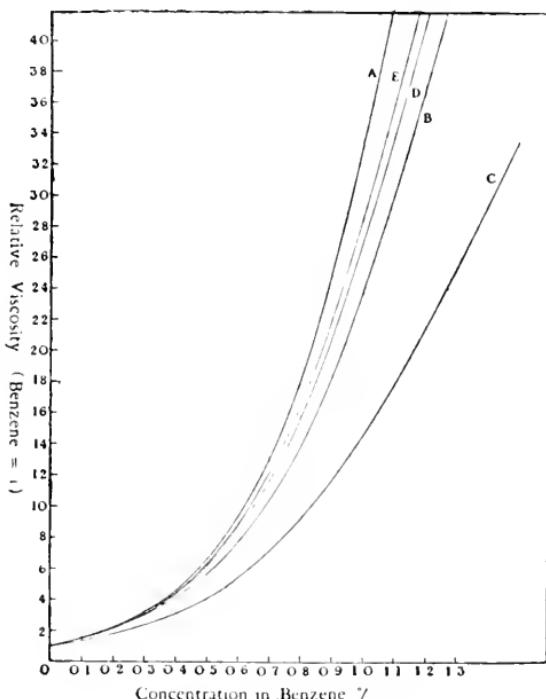


FIG. 5.—Viscosity Curves of Plantation Rubbers

*Nature of Rubber*

*Viscosity*

A=	Plantation old trees, block . . . .	10,000
B=	“ , thick crêpe . . . .	7,700
C=	“ , young trees, thin crêpe . . . .	4,400
D=	“ , biscuit . . . .	8,800
E=	Fine Para, rather poor and old . . . .	9,000
	(Fine Para, good specimen, 12,000-14,000)	

apparatus being standardized to the rate of flow of benzene. The standard method of making the solutions is at room temperature, for we have found that although heating affects the viscosity only slightly in some cases, a very material effect is observable in others; at present we are not in a position to state whether this variability is specific or

accidental. As a general rule, at least three determinations

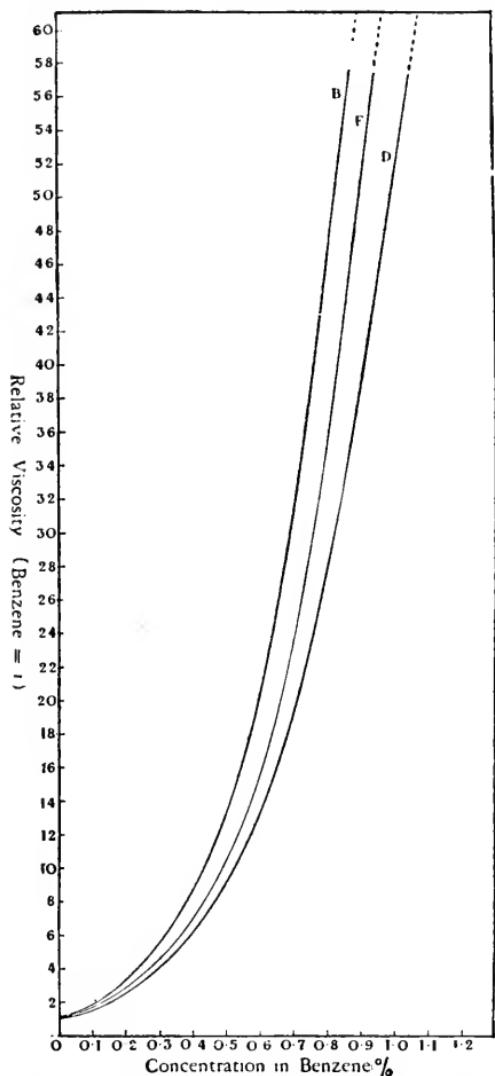


FIG. 6.—Viscosity Curves of *Funtumia elastica* (Different Methods of Coagulation, see p. 163)

Method	Viscosity
B . . . . .	17,000
F . . . . .	17,400
D . . . . .	12,800

the rubber itself. Since the publication referred to was

are made with each rubber, namely, at concentrations of approximately 0.25, 0.5, and 1 per cent., and the concentration is accurately ascertained by evaporation on an aliquot part of the liquid.

If rate of flow—taking benzene as the unit—is plotted against concentration, curves are obtained (see Figs. 4-9) which above a certain point—which we have called the critical point—become approximately linear. In the belief that this approximation to a straight line was very close, we suggested (*loc. cit.*) that the viscosity of the rubber as such might be deduced by employing the linear equation  $y=mx+c$ , and inserting (after  $m$  and  $c$  are determined)  $x=100$ , and so obtaining the viscosity of a hypothetical 100 per cent. solution, *i.e.* of

published, a further mathematical and graphic consideration of the subject has shown that the curves do not approximate as closely to a straight line as we had imagined, and that this is more marked in some cases than in others. The method we now employ is to draw a tangent to the curve at a concentration of 1 per cent.<sup>1</sup> and to take the value of this tangent on a standard scale, namely, 1 cm.=2 viscosity units, and 0.1 per cent. concentration respectively. The value of  $x \times 2000$  gives results which approximate to those obtained by the original method. The values mentioned in this book are worked out in this manner.

### *Effect of Temperature on Viscosity*

The standard temperature of measurement must be rigidly adhered to, a deviation of  $1^{\circ} +$  or  $-$  producing, at a

EFFECT OF HEATING IN SOLUTION ON VISCOSITY

Reference No.	Species.	Description.	Notes on Solution.	Viscosity.	Viscosity after Heating 2 hrs. on a Water Bath.
A	<i>Hevea</i>	From old trees (block)	Practically no insoluble matter. Light colour.	10,000	7,450
B	<i>Hevea</i>	From old trees (thick crêpe)	Practically no insoluble matter. Light colour.	7,700	4,968
C	<i>Hevea</i>	From young trees (thin crepe)	Practically no insoluble matter. Slightly brownish yellow.	4,400	3,179
D	<i>Hevea</i>	From young trees (biscuit)	A good deal of insoluble matter. Light colour.	8,800	4,273
E	<i>Hevea</i>	Washed and crêped fine hard Para	A good deal of insoluble matter. Distinct yellow.	9,000	9,340

concentration of 0.87 per cent., an error of approximately one unit in the relative viscosity of the *solution*. The effect of

<sup>1</sup> This, in the vast majority of cases, is well above what we may still, for practical purposes, call the "critical point."

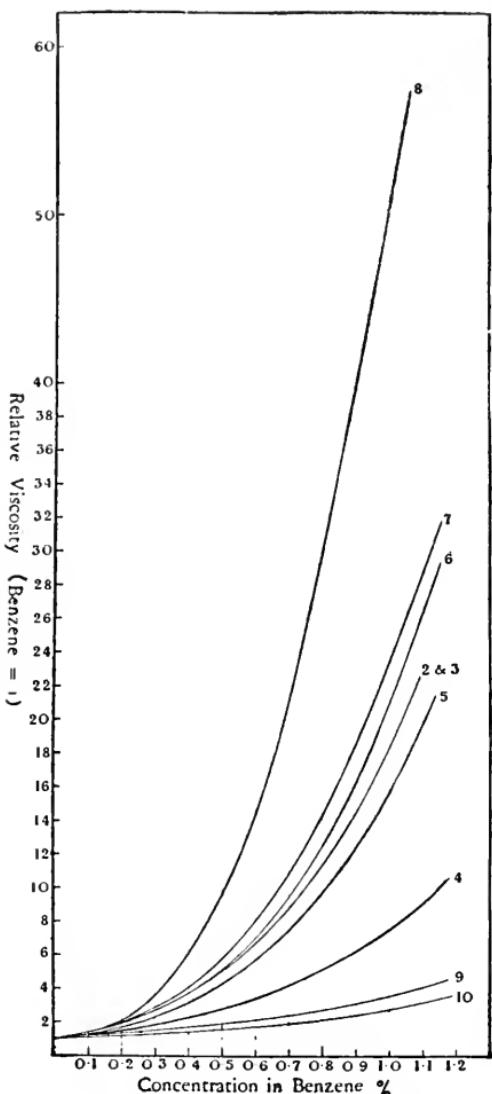


FIG. 7.—Viscosity Curves of Various Rubbers  
(see p. 163)

Nature						Viscosity
2 and 3. Madagascar . . . . .						4,000
4. " . . . . .						1,400
5. " . . . . .						3,800
6. " . . . . .						5,000
7. Zanzibar . . . . .						5,000
8. E. African Thimbles . . . . .						10,800
9. Assam . . . . .						400
10. " . . . . .						500

heating rubber solutions is variable, for while it was found (Figs. 8 and 9) that a sample of rubber from a 30-year old Ceylon *Hevea* and also a sample of *F. elastica* from an old forest tree actually increased in viscosity after heating for two hours on a water bath, a number of plantation rubbers in another series examined, all showed material decreases under the same treatment. The original (*i.e.* before heating) viscosity curves of these rubbers are shown in Fig. 4. The particulars regarding this series are given on p. 161.

It will be noted that the fine Para (a distinctly poor and old sample) showed an increase.

#### Effect of Deresination

Deresination generally increased (cf. Figs. 8 and 9) viscosity. The figures obtained indicated that the higher the resin content the

greater the increase in viscosity after deresination, Nos. 1, 2, and 17 containing a high, 10 and 19 a medium, 13 and 29 a low percentage of resin.

#### EFFECT OF DERESINATION ON VISCOSITY

Reference No.	Species.	Viscosity.	Viscosity after Deresinification.
1.	<i>Funtumia elastica</i> . . . . .	14,913	20,588
2.	" " . . . . .	14,415	17,702
10.	" " . . . . .	15,709	17,896
13.	" " . . . . .	15,211	15,521
17.	" " . . . . .	9,045	11,136
19.	" " . . . . .	15,300	14,524
29.	" Plantation, smoked . . . . .	9,045	9,347
	Fine Para (good specimen, soft cure)	7,552	4,990
		12,524	...

Here again it will be noticed that the only sample showing a material *decrease* is the plantation Para. This is probably due to the effect of heating being greater than the (probable) increase due to deresination.

*Variation according to Species.*—The effect of age and nature of material is illustrated by Figs. 4 to 9. The enormous variation between high class well-prepared rubbers and low grade material is well illustrated by the curves. Whereas *Funtumia* runs up to 18,000 and over, fine Para to about 12,000–14,000, and plantation Para to 10,000–12,000, low grade Assam runs down to 400. The effect probably due to the age of the tree is visible in Figs. 4 and 5.

*Method of Coagulation.*—The effect of the method of coagulation is illustrated by Fig. 6. Three different methods were employed, and on calculating the results it was found that method B gave a viscosity of 17,000, F 17,400, and D 12,800. In another series (*F. elastica*) we found that the variation, using ten different methods of coagulation, was between 11,400 (lowest) and 18,500 (highest).

#### Relationship between Strength or "Nerve," and Viscosity

The strength of crude rubbers may be regarded as composed of three factors—(a) Mechanical structure, (b) physical

structure, (c) chemical structure. As an illustration of "mechanical" structure, I refer, for instance, to the film structure of fine Para, due to the method of coagulation,

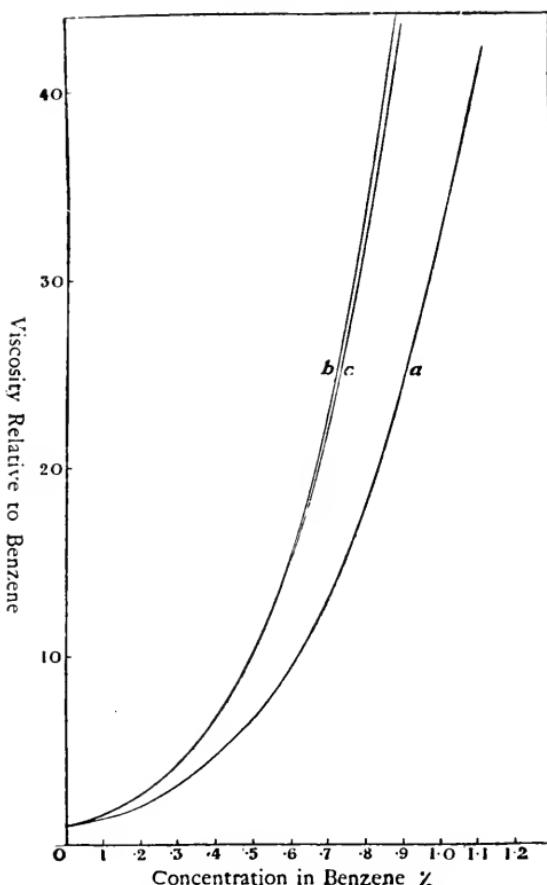


FIG. 8.—Viscosity Curves of Rubber from 30 year old Plantation Trees

The curves show the effect of heating (in solution) and of deresinification (see p. 162)

Nature	Viscosity
a=Original sample . . . . .	9,500
b= , , heated . . . . .	13,200
c= , , deresinified . . . . .	12,600

pulling" tests. The exact relationship of viscosity to physical aggregation and molecular complexity is still uncertain, but that a relationship exists is obvious from purely

and to the network of fibroid proteid matter present in Para and in some other cases. This "mechanical" structure is probably of little direct utility, as it is very largely broken upon the washing and mixing rolls. By "physical structure" I mean the state of colloidal aggregation of the rubber mass. By "chemical structure" I refer to the state of polymerization of the rubber molecule. Viscosity measurements obviously do not connote "mechanical structure," and in this regard, therefore, are greatly to be preferred to "hand-

theoretical reasons, and in practice this relationship, even if we are at present only able to measure it in a rough and ready way, has proved to be of great value. To state my own experience briefly, it is this. Within the same species,<sup>1</sup> viscosity measurements give a direct line as to strength and vulcanizing capacity. Comparing species with species this does not hold good directly, probably because different species possess differently constituted molecules, and the relationship is therefore of a more complex order than as between different specimens of the same species. At the same time, the broad proposition holds good for all species, compared *inter se* or otherwise, that high viscosity figures indicate strength, low viscosity figures weakness.

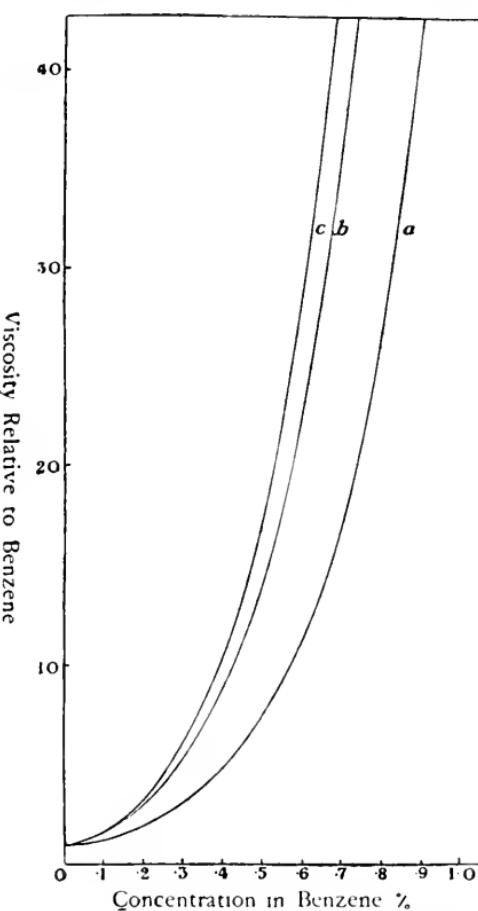


FIG. 9.—Viscosity Curves of *Funtumia elastica*  
The curves show the effect of heating (in solution) and of deresinification (see p. 162)

Nature	Viscosity
a=Original sample . . . .	16,600
b= , , heated . . . .	17,700
c= , , deresinified . .	18,500

<sup>1</sup> Messrs. Frank and Marckwald (cf. ref. p. 131) have recently examined an extensive series of *Manihot* and *Funtumia* samples prepared in different ways, chemically, for "viscosity" and by vulcanization. The results obtained are important and interesting, but, as far as "viscosity" is concerned, the same remarks (see p. 157) apply substantially to their work as to that of Axelrod.

## CHAPTER XI

### THE THEORY OF VULCANIZATION<sup>1</sup>

IN Chapter I. I referred to the importance of the process of vulcanization to the rubber industry. It is no exaggeration to say that, but for the remarkable behaviour of rubber towards and with sulphur and sulphur derivatives, there would be no rubber industry worthy of the name. Practical methods of vulcanization will be discussed in the succeeding chapter, but as the whole subject is so important and our knowledge of it relatively scanty, I make no apology for devoting a special chapter to a consideration of the underlying theory. There are two main methods of vulcanization—(a) *Hot vulcanization*, which consists in exposing rubber to the action of sulphur (as such) and heat; and (b) *cold vulcanization*, or the action of (dilute) sulphur chloride ( $S_2Cl_2$ ) in the cold.

#### HOT VULCANIZATION

Prior to Weber's classical work on this subject,<sup>2</sup> no serious experimental research on vulcanization had been carried out. In the first place he pointed out that the process could not be one of substitution (as suggested by Payen and others), for the simple reason that if this were the

<sup>1</sup> The discovery of "vulcanization" by Goodyear and Hancock respectively has been so exhaustively treated in other works (cf. Weber, *The Chemistry of Rubber*) that I do not propose to enlarge upon the brief historical data mentioned in Chapter I.

<sup>2</sup> *Outlines of a Theory of Vulcanization*, *op. cit.*  
166

case, rubber factories would reek of sulphuretted hydrogen. As a matter of fact, this gas is very rarely in evidence in a work, and when its odour is noticed it is evidence of "something wrong." The result of Weber's work may be briefly summarized as follows :—

*1. The amount of sulphur that enters into combination with rubber, i.e. the combined sulphur,<sup>1</sup> increases with time and rise of temperature.*—This combination is not a linear function, the curves (especially in the case of Para) showing curious kinks at more or less regular intervals. It has been erroneously stated<sup>2</sup> that Weber regarded these kinks as corresponding to the formation of definite chemical compounds, but as a matter of fact he stated (*op. cit.*, p. 89) that they (*i.e.* the kinks) "may be taken as probably indicating a particular physical, rather than some definite chemical, condition of the vulcanized product." He based this view on the fact that if vulcanization is carried out at different temperatures, the kinks appear at different places. At lower temperatures the appearance of the kinks is delayed. Axelrod,<sup>3</sup> on the basis of experimental work which will be referred to subsequently, explains the kinks by the assumption that vulcanization consists of two distinct processes—(1) The action of heat on the rubber which tends to "depolymerize" it, and (2) the entry of sulphur into the molecule which tends to increase the molecular complexity. These two processes do not go hand in hand, but are maximal and minimal in their effect at certain intervals. When the "depolymerization" due to heat has proceeded to a certain point, the material is in a favourable condition for a fresh sulphur "attack," and at this point a kink occurs.

*2. If temperature and time are kept constant, the amount of sulphur entering the molecule is dependent on the quantity originally present.*

<sup>1</sup> Estimated by extracting the vulcanized sample with acetone to remove *free* sulphur and subsequently determining the "combined" by Carius' method.

<sup>2</sup> Hinrichsen and Memmler, *op. cit.*, p. 65.

<sup>3</sup> *G.Z.*, 1909, vol. xxiv. pp. 352-354.

3. Finding that the important changes produced by vulcanization are not clearly apparent until the vulcanized article contains 2 to 2.5 per cent. of combined sulphur, which would correspond roughly to  $(C_{10}H_{16})_{10}S_2$ , and that samples of ebonite<sup>1</sup> prepared with 50, 75 and 100 per cent. of sulphur all gave products containing approximately 32 per cent. of combined sulphur—corresponding roughly to  $C_{10}H_{16}S_2$ —Weber concluded that there exists a whole series of vulcanization bodies of which  $(C_{10}H_{16})_{10}S_2$  is the lowest member, and  $C_{10}H_{16}S_2$  the highest. It is characteristic that, as the combined sulphur increases, the distensibility of the rubber decreases and the tensile strength is heightened. It is necessary to state that Weber's theory is founded on a very slender experimental basis, and that some of his experimental methods, as described, are not entirely convincing. We should, however, remember that he was the first to evolve some sort of order out of chaos, and to lay the foundation for future rational research.

Erdmann<sup>2</sup> suggests that, as at 160° (practically the upper limit of vulcanization temperatures) melted sulphur contains a large proportion of "thiozonide" ( $S_3$ ) molecules, and that as "thiozonide" readily polymerizes to an eight ring, it is likely that the latter would be readily miscible with another eight ring (such as rubber is, according to Harries), and that after admixture has taken place a chemical attack resulting in the formation of rubber thiozonides—corresponding to the well-known ozonides—would ensue.

### *Stern's Experiments*

With a view to re-investigating the phenomena of hot vulcanization by the aid of the methods of modern physical and particularly of colloidal chemistry, E. Stern<sup>3</sup> has made a number of interesting experiments at the Königl.

<sup>1</sup> Ebonite is the product obtained if vulcanization is carried (by using large quantities of sulphur, prolonged time, and high temperature) to the ultimate practical limit.

<sup>2</sup> Liebig's *Annalen*, 1908, 362, p. 133.

<sup>3</sup> *Chem. Zeit.*, 1909, p. 756.

Materialprüfungsamt. The work published so far deals only with the results obtained when using a large excess of sulphur. In order to eliminate the complex mechanical and physical conditions inseparable from vulcanization experiment conducted on ordinary lines, Stern worked with *solutions* of rubber and sulphur in naphthaline. The latter, on account of its high boiling point, chemical indifference, and great capacity as a solvent for the materials in question, etc., is peculiarly suitable for this purpose. Attempts were made, in the first instance, to measure the degree of sulphur combination by determining, at intervals, the melting point of the system,<sup>1</sup> but although it was found that the melting point gradually rose, the differences were too small to admit of accurate interpretation. Stern, therefore, adopted a method of direct analysis, which consisted in withdrawing, with suitable precautions, a sample at intervals, eliminating the naphthalin and free sulphur by means of acetone, and estimating the combined sulphur in the residue. The results obtained by Stern were briefly as follow:—

1. *Quantity of Sulphur.*—Using a large excess of sulphur (from 120 to 239 per cent. of the weight of the rubber) and keeping the time (one hour) and temperature ( $150^{\circ}$ ) constant, the amount of sulphur entering into combination is very nearly proportional to the quantity of sulphur used.

2. *Effect of Time.*—Using again a large excess of sulphur (6 grms. for 5.07 grms. of Para and 90 grms. of naphthalin), and a temperature of  $150^{\circ}$ , it was found that the combined sulphur was practically proportional to the time.

It must be remembered that Stern's published experiments so far cover only a limited range of ground, and that no end points were reached. An exhaustive series of experiments on these lines should, however, give invaluable results.

<sup>1</sup> It was assumed that the depressing effect of the rubber would be practically nil, and that the sulphur which had entered the combined state would also be in a purely "colloidal" state and have no effect. In measure, therefore, as the sulphur combined, the melting point would be raised.

*Axelrod's Experiments*

*Effect of Treatment prior to Vulcanization.*—The extreme importance of the physical condition of rubber in regard to its vulcanizing capacity is well illustrated by the following experiment:<sup>1</sup>—A sample of washed fine Para was divided into two parts A and B—A was not treated in any way, but B was heated for thirty minutes at 120°. The “viscosities” of A and B were determined and found to be, roughly, as 8 : 5. The samples were then each mixed with 10 per cent. of sulphur and vulcanized in the same mould. After vulcanization it was found that B contained 0.16 per cent. more combined sulphur and 0.32 per cent. more resin than A. The tensile properties<sup>2</sup> of the two samples were found to exhibit many material differences, which were as follow:—

To Produce an Extension of	Required a Load of	
	For A	For B
mm.	kg.	kg.
100	1.76	1.09
300	3.09	2.67
500	8.91	6.83
640	25.00	...
665	broke	23.58 (broke)

From the above facts Axelrod argues that as rubber is heated during vulcanization, similar changes (*i.e.* disaggregation and heightening of the capacity for absorbing sulphur) must take place in the course of that process, and that therefore rubbers containing the same amount of combined sulphur, but vulcanized at different temperatures, must possess different physical properties. That this is actually the case is shown by the subjoined figures, which refer to

<sup>1</sup> Axelrod, *G.Z.*, 1909, vol. xxiv. p. 352.

<sup>2</sup> Determined by the Schopper apparatus.

samples of the same mixing vulcanized at  $130^{\circ}$  and  $135^{\circ}\text{C}$ . respectively.

Combined Sulphur.	Vulcanized at $130^{\circ}$ .		Vulcanized at $135^{\circ}$ .	
	Load necessary to produce an Elongation of 600 mm.	Extension at a load of 10 kos.	Load necessary to produce an Elongation of 600 mm.	Extension at a load of 10 kos.
Per cent.	kos.	mm.	kos.	mm.
1	4.7	710	—	—
2	8.6	618	8.3	635
3	14.8	455	11.5	575
4	32.2	400	25.5	480

I have already referred to the fact (p. 167) that Axelrod (on the basis of the above experiments) explained the kinks on Weber's vulcanization curves, in an interesting and reasonable manner.

According to Hübener,<sup>1</sup> the end product of vulcaniza-

tion is a disulphide SS or more probably

SS. An intermediate product, a mono-

sulphide S, also forms. Soft rubbers and com-

mercial ebonite consist of mixtures of unvulcanized rubber and of the mono- and di-sulphide. Hübener arrived at these results by means of a somewhat complicated method of analysis, which will be referred to in another place (see p. 264).

<sup>1</sup> G.Z., 1910, xxiv. p. 627, and J.S.C.I., 1910, p. 289.

*Bysow's Experiments*

Bysow,<sup>1</sup> examining vulcanization phenomena from the point of view of the adsorption theory, found that with a total sulphur content varying from 4.34 per cent. to 9.27 per cent., the ratio Total : Free sulphur is independent of the total, but dependent on the vulcanizing conditions. For small quantities of total sulphur, *i.e.* for 1 per cent. to 2 per cent., the ratio follows the exponential formula—

$$\frac{\text{Total S}^n}{\text{Free S}} = K.$$

For two hours (live steam cure) at 45 lb.,  $n = 3.1$ .

Bysow further found that with a total sulphur of from 3.44 per cent. to 8.91 per cent. equilibrium was not produced until the samples were over-vulcanized, and that under these conditions the ratio Total : Free sulphur decreases with an increasing total sulphur.

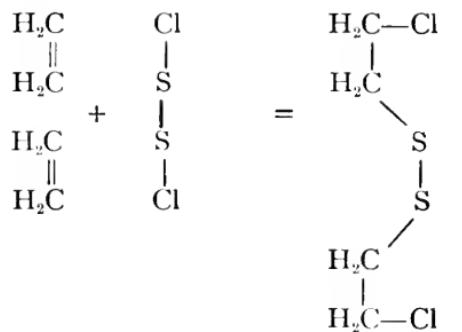
*Effect of Time.*—Working in live steam, at 50 lb., over periods of from 40 to 150 minutes and with 3.5 per cent. total sulphur, the free sulphur was found to vary from 1.90 per cent. to 0.19 per cent.; and a curve was obtained which tends to show that the free sulphur does not become constant until after the (technical) vulcanization optimum has been passed.

Broadly speaking, Bysow's work indicates that in the primary stages vulcanization is a purely physical (adsorption) process, but that at a later stage a chemical reaction takes place. Recent work on cold "vulcanization" (see p. 177) points in the same direction. The work of Bysow and that of Axelrod respectively may be brought into line by assuming that sulphur adsorption goes hand in hand with the colloidal disaggregation produced by heat, and that when a certain quantity of sulphur has been adsorbed, chemical reaction takes place, and, as a result, the state of aggregation becomes more complex.

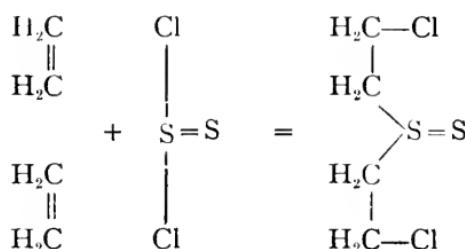
<sup>1</sup> Z.K., 1910, vol. vii. p. 160.

## COLD VULCANIZATION

The study of "cold curing" resolves itself for practical purposes into an investigation of the action of dilute sulphur chloride solutions on rubber or rubber solutions. The methods of scientific investigation approximate, therefore, more closely to technical conditions, than can possibly be the case in regard to hot vulcanization. The problem, however, is somewhat complicated by the chlorine factor. Modern theories regarding cold curing are founded on, or, perhaps to be more accurate, arise out of, the work of Henriquez,<sup>1</sup> who showed that the reaction with sulphur chloride is purely additive. This was confirmed by Weber,<sup>2</sup> who suggested that the chloro-sulphides formed are saturated products similar to those investigated by Guthrie,<sup>3</sup> and that the reaction takes place on the following lines:—



or



<sup>1</sup> *Chem. Zeit.*, 1893, vol. xvii. p. 634; 1894, vol. xviii. pp. 701 and 1155. Cf also Hinrichsen and Memmler, *op. cit.*, pp. 54 *et seq.*

<sup>2</sup> *The Chemistry of India-Rubber*, p. 97, and *J.S.C.I.* 1894.

<sup>3</sup> *Annalen*, 1860, vol. cxiii. p. 270.

By allowing an excess of  $S_2Cl_2$  to act on rubber in benzene solution, Weber obtained a substance which, after washing and extraction with  $CS_2$ , gave on analysis figures corresponding closely to  $(C_{10}H_{16}S_2Cl_2)_n$ . This body Weber assumed to be the ultimate product of cold vulcanization, but he afforded no convincing proof that it was homogeneous. A further series of experiments in which a large quantity of rubber and a small quantity of  $S_2Cl_2$  were employed, yielded a product from which no rubber could be separated, and corresponding on analysis to  $(C_{10}H_{16})_{24}S_2Cl_2$ . Weber concluded that by the action of  $S_2Cl_2$  on rubber a series of chloro-sulphides, ranging from  $(C_{10}H_{16})_{24}S_2Cl_2$  to  $(C_{10}H_{16}S_2Cl_2)_{24}$ , are formed.

Although, as Hinrichsen has recently pointed out, Weber's theory was subjected to a very damaging criticism by Henriquez very shortly after its appearance (1894),<sup>1</sup> it was very generally accepted, and has even in comparatively recent times been used as the basis of the structural formula and of further views concerning the nature of the chloro-sulphides.

#### *Work of Hinrichsen, Meisenburg, and Kindscher*

These authors have recently<sup>2</sup> reinvestigated part of the ground covered by Weber, but were quite unable to confirm the results obtained by him. Working in the same manner as Weber and with an excess of  $S_2Cl_2$  greater than that used in his experiments, they obtained products containing from 15.58 per cent. to 28.37 per cent. of sulphur, and could find no evidence of any regularity in the results. It will be observed that the sulphur maxima and minima are materially above and below the figures obtained by Weber. They

<sup>1</sup> Henriquez, *Chem. Zeit.*, vol. xviii. pp. 701 and 1155, pointed out that the amounts of chlorine and sulphur found in Weber's products practically correspond to the amount of  $S_2Cl_2$  used, and that there was no proof of their homogeneity. Henriquez was able to obtain chloro-sulphides containing from 36.35 per cent. to 24.16 per cent. of sulphur, whereas the maximum amount found by Weber was 23.63 per cent.

<sup>2</sup> *Chem. Zeit.*, 1909, vol. xxxiii. p. 736, and *Z.K.*, 1910, vol. vi. p. 202.

suggest that if a definite "end product" is obtained by this method, its sulphur content probably approximates to one of the lower figures obtained by them, inasmuch as it is extremely difficult to remove the adsorbed excess of  $S_2Cl_2$ , and the sulphur set free by traces of moisture from the latter is present in an extremely insoluble form.

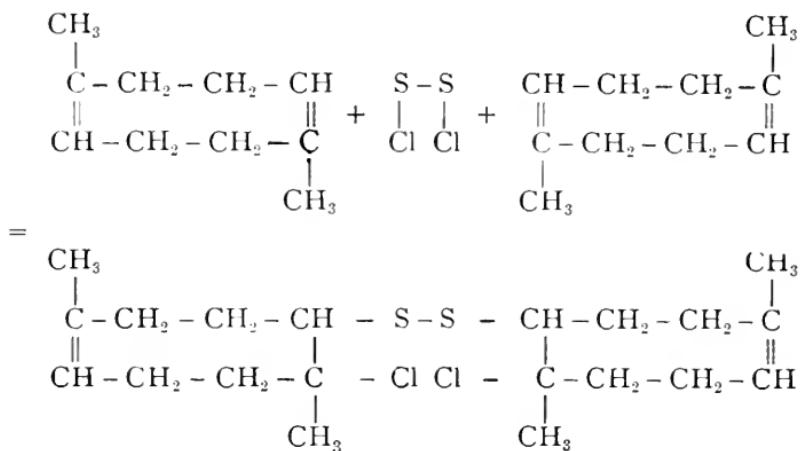
Hinrichsen and his colleagues next proceeded on novel lines to investigate the question whether a definite compound forms or whether the reaction between rubber and  $S_2Cl_2$  is an adsorption process. This they did by the method of indirect analysis, which, as experience has shown, is the only reliable one in connexion with colloidal reactions. They added definite quantities of  $S_2Cl_2$  dissolved in benzene to rubber solutions in the same solvent, particular care being taken to exclude any trace of moisture, and then examined, not the products of reaction, but the remanent liquors. From the estimation of chlorine in the latter, the quantity of  $S_2Cl_2$  that had entered into reaction or had been adsorbed was calculated. Using a constant quantity of rubber and varying the amount of  $S_2Cl_2$  solution, it would follow, if a definite chemical reaction takes place, that the quantity of  $S_2Cl_2$  disappearing would remain constant, whereas if the reaction is purely physical (*i.e.* an adsorption phenomenon), the concentration of the system would be the main factor, and the reaction would take place according to the exponential formula :—

$$\frac{X}{\alpha} = K \cdot c^n,$$

in which X represents the quantity of  $S_2Cl_2$  used;  $c$  the concentration of the  $S_2Cl_2$  solution at the beginning of the reaction;  $\alpha$  the concentration of the rubber; and K and n are constants.

The results obtained, using 0.5 grms. of rubber in each case and quantities of  $S_2Cl_2$  varying between 0.4330 grm. and 1.2990 grm., showed that a practically constant amount (the range in eight experiments was from 0.2552 grm. to

0.2644 grm.) of  $S_2Cl_2$  disappears, and it is therefore more than probable that the reaction is purely chemical.<sup>1</sup> To this extent, therefore, Hinrichsen agrees with Weber, but his experiments point clearly to the formation of a compound  $(C_{10}H_{16})_2S_2Cl_2$ , and not to  $C_{10}H_{16}S_2Cl_2$  as believed by the earlier worker. The formation of the body assumed by Hinrichsen is readily explained on the basis of Guthrie's researches as follows:—



With alcoholic soda this body splits off 2 molecules of  $HCl$ , a substance free from chlorine and containing 20.7 per cent. of sulphur (theory 19.2 per cent. for  $(C_{10}H_{15})_2S_2$ ) forming. The corresponding product obtained by Weber contained 32.3 per cent. of sulphur and was believed by him to be  $C_{10}H_{14}S_2$ .

No definite conclusion can yet be drawn regarding the

<sup>1</sup> Ostwald (see p. 179) has pointed out that at high concentrations—such as those at which Hinrichsen worked—the adsorption curve generally tends to become less and less dependent on the concentration, and that in view of this fact and of the results obtained by Bysow (see p. 177) at low concentrations, the inferences drawn by Hinrichsen are open to criticism. It is, however, equally reasonable to suggest that the known facts are best explained and reconciled by assuming that at low concentrations and in the initial stages at high concentrations, the reaction is an adsorptive one, and that it subsequently becomes chemical. There must necessarily be a certain amount of "overlapping," probably more accentuated at high than at low concentrations.

composition of technical cold cured goods. Hinrichsen suggests that they consist of solid or semi-solid solutions of the "end product" in rubber, and that this solid solution contains varying quantities of adsorbed "free sulphur."<sup>1</sup>

### *Experiments at low Concentrations*

Working with 0.6 per cent. to 3.6 per cent. of  $S_2Cl_2$  in 100 c.c. light petroleum and with thin Para strips weighing about 0.5 grm., Bysow<sup>2</sup> found after thirty minutes' exposure that the combined sulphur was practically proportional to the concentration of the solution. The curve was practically linear. It was found, however, that under the time condition of the experiments, the reaction was not completed. For instance, in the case of the solution containing 1.8 per cent.  $S_2Cl_2$ , the combined sulphur (in the rubber) after thirty minutes (the period of time on which the curve referred to above was based) amounted to 2.96 per cent., whereas at the end of sixty minutes this figure had risen to 4.73 per cent., and the reaction was obviously still not complete. Bysow next determined the time occupied to reach equilibrium for a much more dilute solution, namely, 0.1 per cent., and found that at the end of one hour constancy was attained. A series of experiments with  $S_2Cl_2$  concentrations varying from 0.0125 per cent. to 0.1 per cent. was then undertaken, two hours being allowed for the establishment of equilibrium. The results obtained were very close to the requirements of theory for the exponential adsorption formula. The curve was found to be of the parabolic type, and from a mean of four determinations the exponential  $n$  was found to equal 1.97. The results of this series of

<sup>1</sup> Hinrichsen showed that the sulphur content of a product obtained by allowing an excess of  $S_2Cl_2$  to act on rubber could be reduced from roughly 28 per cent. to 24 per cent. by extraction with  $CS_2$ , and that by a further treatment with ammonium sulphide this could be lowered to (in round numbers) 19 per cent. It is obvious, therefore, that a considerable proportion of the "free" sulphur is not present in a purely mechanical form.

<sup>2</sup> Z.K., 1910, vol. vi. p. 281.

experiments are of sufficient interest and importance to be quoted *in extenso*, and are as follow:—

Concentration of $S_2Cl_2$ .	S. Found.	S. Theoretical (for adsorption formula).
Per cent.	Per cent.	Per cent.
0.0125	0.17	0.16
0.025	0.21	0.22
0.0375	0.25	0.28
0.05	0.36	0.32
0.075	0.41	0.39
0.1	0.45	0.45

Bysow was also able to show that the further requirement for absolute proof that the process is one of adsorption, namely, that only the concentration and not the absolute quantities are of import, holds good. The figures obtained by him were as follow:—

Rubber (quantity).	Volume of Solution.	$S_2Cl_2$ in Solution.	Combined Sulphur.
grms.	cc.	grms.	Per cent.
0.5	100	0.1	0.45
0.5	200	0.2	0.47
1.0	100	0.1	0.50

Under the conditions of these experiments Bysow found that sulphur and chlorine were adsorbed in equivalent quantities, but a later paper<sup>1</sup> he records results which appear to cast serious doubts on Weber's hypothesis to this effect. From Bysow's experiments it is to be gathered that the amount of sulphur entering into combination depends largely on the purity of the  $S_2Cl_2$ , and that the combined sulphur increases according to the quantity of free sulphur

<sup>1</sup> Z.K., 1911, vol. viii. p. 47.

present in the  $S_2Cl_2$  solution. The experiments referred to are, however, not convincing, particularly as the rubber worked with contained 0.66 per cent. of moisture.

### *Wo. Ostwald's views on Vulcanization*

#### *The Adsorption Hypothesis*

In a most interesting and suggestive series of papers<sup>1</sup> Wo. Ostwald sets forth a number of facts and inferences which tend, according to him, to show that vulcanization—both hot and cold—may after all not represent a chemical reaction, but that the known phenomena may be equally well, and in some respects better, explained by the assumption that the process is one of colloidal adsorption. The main points in Ostwald's argument are as follow:—

(a) It is admitted that every vulcanized rubber contains a certain amount of "free" sulphur, and that (according to Höhn, *loc. cit.*) it is difficult to reach finality in regard to the extraction of the free sulphur.

(b) It is admitted that the sulphur forms only additive and not substitution products. Weber's theory of a series of compounds starting with a body containing about 2.5 per cent. sulphur and ending with one with 32 per cent. is difficult to explain chemically, and so far it has not been possible to confirm Weber's views regarding the "beginning" and "end" products. I have already explained elsewhere (see p. 176) why Ostwald does not regard the apparently definite chemical product of cold vulcanization obtained by Hinrichsen and his colleagues as detrimental to his hypothesis.

(c) The process is apparently reversible, for if vulcanized rubber is treated for prolonged periods with successive fresh quantities of solvents, it becomes increasingly soluble and more and more sulphur is extracted. In reply to this I think it is fair criticism to say that reversibility of a reaction does not necessarily imply that it is of an adsorptive

<sup>1</sup> *Z.K.*, 1910, vol. vi. p. 136; *ibid.*, vol. vii. p. 45.

character, and that in the case of a huge molecular aggregation, such as rubber appears to represent, a breaking down of its structure by prolonged heat is by no means out of the question.

(d) He refers to Axelrod's work (see p. 167) and to the well-known fact that the more rubber is mechanically worked the more readily it takes up sulphur. I cannot see that this fact tells in any way against the chemical theory or in favour of the adsorption hypothesis. If, as appears undoubtedly to be the case, mechanical working causes physical disaggregation or lessening of molecular complexity, or both, it may surely be assumed that conditions more favourable to a chemical sulphur attack are thereby brought about.

(e) According to Van't Hoff's temperature law, an increase of  $10^{\circ}$  should increase the rapidity of chemical reaction 2 to 3.5 times. Weber's vulcanization experiments indicate that the average coefficient of increase is 1.87, a figure very similar to that obtained for some adsorption reactions. For instance, Bayliss found for the adsorption of Congo red by filter paper the figure of 1.36. The kinks on Weber's vulcanization curves are, according to Ostwald, very similar to those seen on hydration curves of other colloids, for instance of silicic acid and of iron hydroxide.

(f) Assuming that vulcanization is a practically irreversible process, this does not necessarily exclude the adsorption theory. He refers to the analogy of the irreversible adsorption of methyl-violet by charcoal.

(g) Recalculating Stern's results (see p. 168) on the basis of the exponential adsorption formula, he finds a maximum difference between theory and actual result of 0.79 per cent., whereas if calculated on a chemical basis the maximum error is 11.6 per cent. Hübener's figures may also be interpreted favourably to the adsorption formula. Interesting as are Ostwald's views, they are scarcely convincing if applied to the complete vulcanization process, either hot or cold. It is extremely likely, as I have already stated, that at the commencement and probably at intervals at definite later

periods, the process or reaction is purely adsorptive, but that otherwise it is mainly chemical.

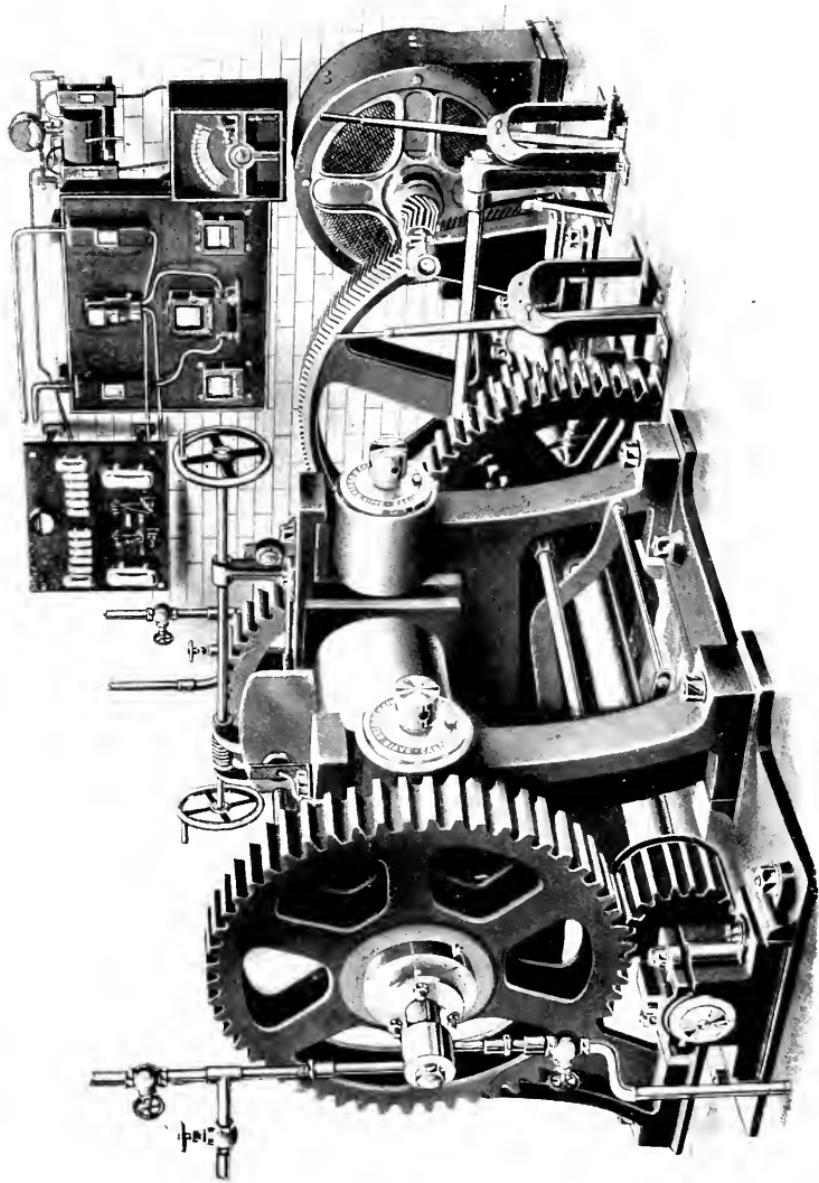
Alexander<sup>1</sup> makes a point which appears to me to be an almost entirely convincing proof of the untenability of Ostwald's views, if taken on their broadest basis. It is that the tetra-bromide and nitrosite derivatives obtainable from vulcanized rubber, which are got by precipitation *from solutions*, contain the whole of the sulphur of vulcanization. If the sulphur is merely adsorbed, why should it come down quantitatively from *solutions* in which it is soluble?

<sup>1</sup> *Chem. Zeit.*, 1910, p. 789.

## CHAPTER XII

### THE MANUFACTURE OF RUBBER GOODS

THE main processes employed in the manufacture of articles from crude rubber may appear at first sight to be of an essentially simple nature, yet there is perhaps no industry in which personal experience and knowledge of small details count for so much. The chief reason for this is that the methods of manufacture are still largely empirical, the reason being partly that the industry is a comparatively young one, and partly because the scientific and technical principles governing manufacture are by no means clearly defined. In making these statements I have no intention of doing that which is so frequently done in connexion with so many other industries, namely, of throwing stones at the manufacturer on the score of conservatism or ignorance. It is evident that in the case of a material possessing such complex chemical and physical properties as india-rubber that true scientific and technical progress must be slow. It is equally true that in this as in other industries technical progress can only come about by the intimate co-operation of the manufacturer with the practical scientific technologist. The main principles governing the manufacture of india-rubber articles, and the methods employed, are substantially the same as they were some twenty or thirty years ago, but there have been innumerable improvements in details both of plant and of methods. I shall endeavour in this chapter to give a brief, and as far as possible connected, account of the general principles governing modern manufacture, and to refer to details only where



MIXER AND GRINDER, DIRECT ELECTRIC DRIVE  
(THE MACHINE IS FITTED WITH TWO GEARS; LOW DIFFERENTIAL FOR MIXING, AND HIGH DIFFERENTIAL FOR GRINDING)



this course is unavoidable. A detailed account of the various branches of rubber manufacturing would fill several large volumes, and it is at least doubtful whether there is any one man living both qualified and in a position to carry out so great an undertaking.

#### *OUTLINE OF MANUFACTURING OPERATIONS*

An india-rubber article in the process of manufacture is subjected to a series of operations which are briefly as follow. First the crude rubber as it arrives at the factory must be purified, and this is done by the process called washing. The washed rubber is subsequently dried. If ordinary mechanical goods are to be made, the next process is that of mixing. This consists of incorporating with the rubber the necessary quantity of sulphur and filling materials. The next step as a rule is that of calendering ; this consists in rolling out the well-mixed and homogeneous dough to sheets of the required thickness. The calendered material passes next to the making-up table, where it is cut to suitable sizes either for the hydraulic vulcanizing press or prepared for the moulds. The next process is that of vulcanizing, which consists substantially in subjecting the calendered dough to combined heat and pressure, or heat only, in the press, in a mould, or in the open. The above process is necessarily varied according to the nature of the goods to be manufactured. For instance in the case of many solid tyres the rubber is not first calendered, but the well-mixed dough is forced through an appropriate die. The same applies to "squirted" tubing. In the case of elastic thread the rubber is mixed with flowers of sulphur and "let down" with a solvent, and the mass so obtained spread or calendered on to cloth. The above remarks refer to goods which are made by the hot process of vulcanization. There is, however, a large class, such as articles made from cut sheet, waterproof goods, and, broadly speaking, all articles in which the rubber layer is thin, which is prepared by the cold process. In this

method the rubber is not first mixed with sulphur and then exposed to heat, but is subjected in the form of a thin layer or sheet to the action of a dilute solution of sulphur chloride in a suitable solvent, or to the action of sulphur chloride vapours. The cold process cannot be applied to goods of any thickness, for the simple reason that the action of sulphur chloride is so powerful that by the time the interior of a piece of rubber of any considerable thickness is properly cured, the outer portions are over-vulcanized. The above does not profess to be more than the merest sketch of the general methods employed, but it has been written so that those not familiar with the industry may more readily understand the remainder of this chapter.

### WASHING

In the above we have seen that the first operation to which the rubber is subjected on entering the factory is that of purification. This purification is carried out by the so-called process of *washing*. The ordinary process of washing consists in passing the rubber, after it has been cut up and soaked in warm water to render it pliable, through corrugated, fluted or diamond-cut rolls working at uneven speeds, and at the same time subjecting the mass to the action of a stream of cold or warm water. This treatment is repeated until mechanical impurities such as sand, bark, small stones and chips of wood have been removed, and a homogeneous sheet of crêpe-like texture is obtained. Works washing rolls are of substantially the same design as those employed for a similar purpose in connexion with the plantation industry (see p. 76), except that they are generally larger and more strongly built, inasmuch as the rubber which comes to the works is tougher—having had time to “set” and harden—than the fresh scrap, not to mention “No. 1 Latex” rubber, dealt with on the plantation. In large works it is not unusual to have a battery of washers, the first geared to a differential speed of about 6:4 with deeply diamond cut or

grooved rolls, the second geared say at 6:5 and with rolls of a less pronounced pattern, the third and last geared to a difference of one tooth and with smooth rolls. This method saves a good deal of time in regard to "setting" the rolls, and tends to produce more homogeneous material. Occasionally three roll washers are employed. It is probable that at no very distant date the washer will practically disappear from the works. The process of washing involves the use of much power and time, and, apart from its actual cleansing effect, it is certainly not beneficial to the rubber. It is now well recognised that the less rubber is subjected to mechanical action the better, for the more it is worked the softer and less resilient it becomes. At the present day already much of the clean plantation rubber is not put through the washing rolls, but is taken to the mixing rolls after a short preliminary drying. In brief, there is no object in washing rubber which is dry and clean and which contains substantially no soluble matter, excepting perhaps in the case of the highest classes of goods, such as cut sheet or elastic thread, where the very highest degree of purity is essential. A novel type of washing-machine (Fig. 10) has lately been introduced by Messrs. Werner, Pfleiderer & Co., which would appear in some respects to have considerable advantages over the old type. In this machine no attention from the workman is necessary. The full charge of rubber is placed in the machine, it is then closed, and the fluted masticators are set to work. It is stated that in a machine of this type 2 to 3 cwt. of rubber can be treated in an hour and that the results are extremely satisfactory.<sup>1</sup> It may be mentioned that in the old type of washing-machine constant attention is necessary, inasmuch as the rubber has to be guided on its way through the machine by the operator. The machine delivers the rubber in the form of thick corrugated lumps or slabs, and this undoubtedly is a disadvantage,

<sup>1</sup> It would appear that as the action is one of kneading rather than of tearing, that the "nerve" of the rubber is much less affected than is the case with the ordinary washing rolls.

as it is necessary, in order to obtain the rubber in a dry sheet in a reasonable time, to pass it through the ordinary washer

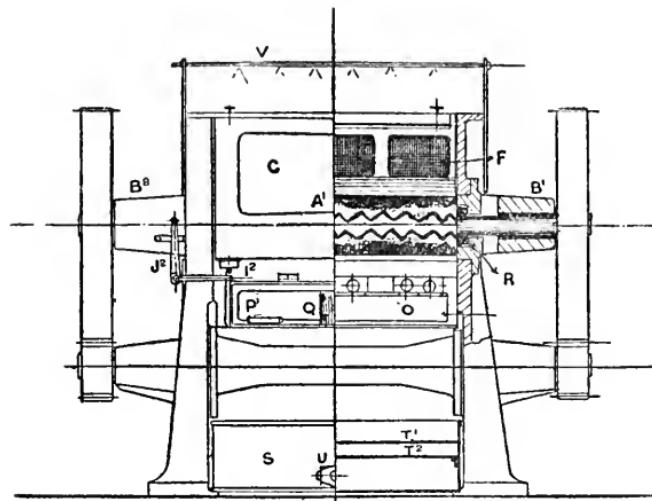


FIG. 10 (A).—Werner-Pfleiderer Washing Machine (see p. 185).

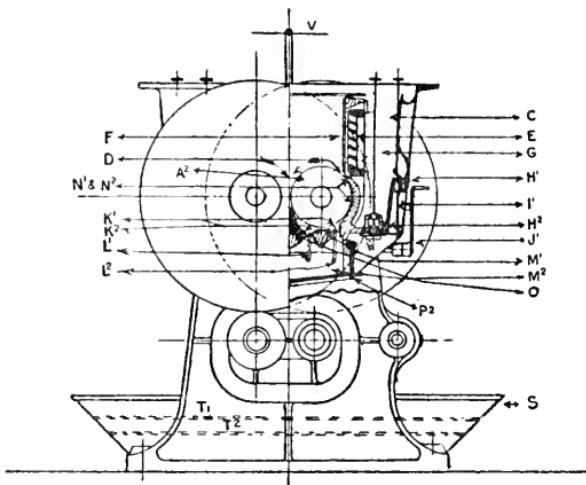


FIG. 10 (B).

Fig. 10 (A) shows a sectional view of the machine taken through the middle from back to front, and Fig. 10 (B) shows the front elevation. A<sup>1</sup> A<sup>2</sup> are deeply corrugated rolls carried in fixed bearings B<sup>1</sup> B<sup>2</sup>. The corrugations do not intermesh, and the peripheries are some distance apart. C is a trough shaped at the bottom to follow the peripheries of the rollers and carrying ledges

D at the back and front so that they turn the rubber over and guide it between the rollers as it is brought to the surface by the action of rollers that run towards one another as shown by the arrows, and catch any large impurities, such as stones and nails. E are gratings set in the sides to allow the lighter impurities to escape, and F are the sliding frames covered with sieves to prevent the escape of particles of rubber. G is a surrounding jacket to the trough which can be drained by valves H<sup>1</sup> H<sup>2</sup>, and outlets I. J<sup>1</sup> is a lever placed on the right hand side of the machine for operating the valve H<sup>1</sup>, and J<sup>2</sup> is a lever placed on the left hand side for operating valve H<sup>2</sup>. Slots K<sup>1</sup> K<sup>2</sup> are provided in the bottom of the trough, immediately beneath the rollers, and in these slots Shakers L<sup>1</sup> L<sup>2</sup> are suspended for the rapid removal of all sand and similar heavy impurities. M<sup>1</sup> and M<sup>2</sup> are ledges in addition to the ledges D upon which the rubber is turned, and N<sup>1</sup> N<sup>2</sup> are saddles upon which the rubber is opened out. O is a sand box that with G completes the water jacket surrounding the trough C. P<sup>1</sup> P<sup>2</sup> are flaps to the sand box O and hinged at the top, so that when open the box can be thoroughly flushed. Q<sup>1</sup> is an outlet in the flat P<sup>1</sup> for draining the sand box O. R is a packing to prevent the escape of water through the ends of the trough C through which the blades of the spindles pass to the bearings B<sup>1</sup> B<sup>2</sup>. S is a straining vessel to catch the impurities and so prevent blockage of the water drains and at the same time to arrest any particles of rubber that may accidentally escape. T<sup>1</sup> T<sup>2</sup> are two sieves in the straining vessel S, and U is an outlet for draining this vessel. V is the water spray pipe. The rubber can be freely fed into the machine, and the rollers acting in conjunction with the peculiarly formed trough carry the rubber down, round and up again continuously and automatically.

or sheeter after cleansing. Nevertheless, there should, I think, be a future for this type of machine, particularly for the cleansing of sandy and dirty rubbers.

### DRYING

The principles of drying factory washed rubber are not quite the same as those which apply to the drying of freshly coagulated rubber.<sup>1</sup> In the latter case the moisture is mainly contained in the "fibre" of the rubber; it appears to be evenly dispersed—possibly in a "colloidal" state—throughout the whole mass. In factory washed rubbers the

<sup>1</sup> Cf. Chap. V. p. 79.

water seems to be—excepting in the case of relatively wet material—chiefly present on the surface of the “fibre.” Surface moisture can be quickly removed, whereas adsorbed or interstitial moisture—if these expressions may be used to express a phenomenon that still requires investigation—is not readily got rid of. While it is more difficult to wash the rubber as it arrives at the factory than on the plantation, it is correspondingly (and for the same reason) easier to dry it. The method of factory drying is very similar to that already described in connexion with the plantation industry. The rubber is hung on racks, preferably in chambers through which a slow current of warm air is passed in a systematic manner. The optimum drying temperature will vary with the type of the rubber, but here again the principle that—as far as the quality of the rubber is concerned—the lower the temperature and the drier the air, the better, holds good. Very low grade, resinous rubbers cannot be dried on racks, but are best laid over canvas-covered frames, beneath and through which the air can circulate. After the rubber is dry it is rolled up and kept in a cool, dark, but reasonably well-ventilated storeroom. I am not aware that the smoke cure has ever been tried in connexion with factory drying, and, as a rule, there could be very little object in this. Where, however, circumstances render it necessary to store washed rubber for any length of time, or where it is difficult to obtain cool storage space, I think this method might be distinctly advantageous.

### MIXING

#### *Materials Employed in the Manufacture of Rubber Goods<sup>1</sup>*

The materials employed in the manufacture of rubber goods consist of rubber, sulphur, and various other organic and inorganic substances. There is a popular belief to the

<sup>1</sup> For a very full account of the various materials employed in rubber mixings, cf. Pearson, *Crude Rubber and Compounding Ingredients* (The India-Rubber World Publishing Co., New York).

effect that rubber goods of high quality should consist of nothing but rubber and sulphur, but, as a matter of fact, a mixing consisting solely of these materials is, apart from the question of cost, not suitable for the majority of commercial articles. For instance, a pneumatic tyre cover, or a solid tyre made solely from rubber and sulphur, would be cut to pieces on the road in a very short time, owing to the comparative softness of a mixing of this type. The materials other than sulphur and rubber which are employed may be classified as follow:—

- (a) "Fillers" or "cheapeners" pure and simple.
- (b) Materials employed for the purpose of imparting a specific quality or qualities (hardness, toughness, resistance to steam, and so on).
- (c) Pigments.

(a) FILLERS.—Powdered chalk, barytes and ground rubber waste may be regarded as typical "cheapeners," possessing little if any valuable specific quality. In many cases such substances as zinc oxide, lithopone, oil "substitutes" and reclaimed rubber are also used solely as cheapeners, but each of these materials may, if rationally employed, serve some useful specific purpose apart from the lowering of cost. Thus zinc oxide hardens and toughens a mixing and increases its resistance to cutting and abrading forces, if used within certain limits and together with otherwise suitable materials. The same remarks apply to lithopone. The oil "substitute" serves to produce rubber goods in which cheapness combined with a low specific gravity and an absence of hardness are required. Good "reclaimed" rubber is a valuable ingredient in mixings which have to be made at a moderate price and in which a large quantity of "minerals" cannot be employed.

(b) MATERIALS USED FOR SPECIFIC PURPOSES.—(i) *For increasing mechanical strength*, or, in other words, for hardening or toughening the goods, minerals such as zinc oxide,

lithopone, magnesia (oxide), lime, litharge, and for special purposes ground glass (for instance for "eraser" rubber) and talc are used. Certain organic substances, for instance balata—which contains a hydrocarbon similar to that of rubber—also possess a toughening effect, without, however, speaking broadly, decreasing the elasticity or rather distensibility of the material to the same extent as "minerals."

(ii) *For making dense, i.e. non-porous, mixings for increasing resistance to water, improving the dielectric properties,* organic materials such as asphalt, bitumen and coal tar pitch are exceedingly useful.

(iii) *For softening harsh mixings, i.e. for cheap goods containing large quantities of minerals such as chalk or barytes, certain oils, and more particularly vaseline, are employed.*

(iv) *For hastening vulcanization, or improving vulcanizing conditions,* such materials as litharge, magnesia, quicklime and antimony sulphide (golden sulphide) are in many cases essential. Goods cured in live steam (see under "Vulcanization," p. 197) are, as a rule, readily vulcanizable with sulphur alone. On the other hand, articles vulcanized in the press or in hot air cure very slowly and unsatisfactorily in the absence of an accelerating agent. Until recently it was generally assumed that the accelerating agents referred to act as sulphur carriers or catalysts, but a recent and most interesting piece of work by E. Seidl<sup>1</sup> appears to prove beyond reasonable doubt that in the case of litharge the hastening effect is due to the heat of the reaction taking place between the oxide and the small quantities of sulphuretted hydrogen produced by the decomposition of the resins and of the proteid matter. The action of the "catalysts" is most pronounced in the case of many softish, resinous rubbers, which are, indeed, practically unvulcanizable in the press if sulphur alone is employed. Litharge can only be employed for the preparation of dark coloured goods owing to the formation of black lead sulphide, but magnesia

<sup>1</sup> G.Z., 1911, vol. xxv. p. 710, and *ibid.*, p. 748.

and lime are available for white or light coloured goods and antimony sulphide for red articles.

(c) PIGMENTS.—The most important white pigments are zinc oxide, lithopone (a compound of zinc sulphide and barium sulphate), barytes, and (for cold-cured goods only) white lead. Antimony sulphide ("golden sulphide") and mercuric sulphide (*vermilion, cinnabar*) are very largely employed as *red* pigments, the latter chiefly in hard rubber, mainly for dental work. Pigments or dyes other than white and red are only employed for special purposes (toys,

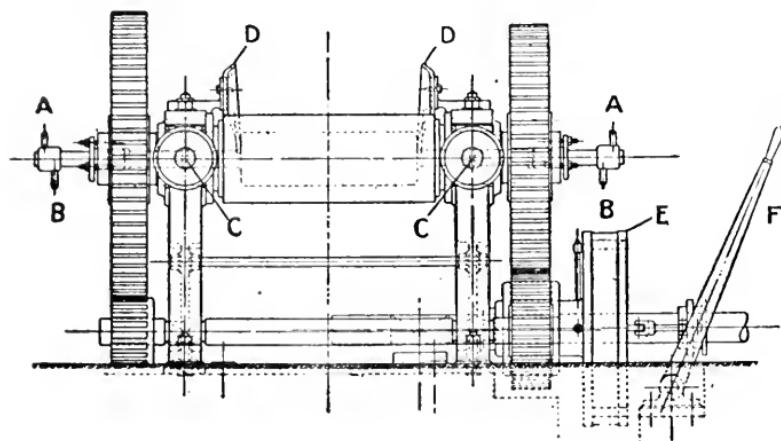


FIG. 11 A.—Mixing Machine, direct drive

(AA, inlets for steam or water; BB, corresponding outlets; CC, adjusting screws; E, friction clutch actuated by lever F)

flooring-tiles and imitation mosaic, fancy waterproof cloths, etc.), and the same applies to lustres and bronzes.<sup>1</sup>

### *The Mixing Operations*

The general construction of the mixing mill is similar to that of the washing rolls. Fig. 11 A shows one of Messrs. Bridge's double-geared mixers of a modern type. The rolls are hollow and are fitted with the necessary connexions for heating by steam or cooling with water. The steam or water,

<sup>1</sup> Cf. Weber, *The Chemistry of India-Rubber*, pp. 201 *et seq.*, and Ditmar, *op. cit.*, pp. 90 *et seq.*

as the case may be, enters at A and passes out at B. The rolls are generally much larger than those of the washer, being made up to 84 inches in length. The usual works size is, however, roughly 35 inches to 45 inches in length by 12 inches to 16 inches in diameter. The gearing is differential, the front or working roll running at about eighteen to twenty, the rear roll at twenty-five to twenty-eight, revolutions. In practice the working roll is kept slightly hotter than the rear roll, and the effect of this and of the differential gearing is that the plastic mixing remains on the front roll. The rolls are set by means of the screws C, and

are provided with guides D, which prevent the mixing from working on to the bearings and from contamination with the lubricants. All modern mixers are provided with some form of safety clutch (in the illustration a friction clutch E actuated by the lever F is shown) with a view to instantaneous dis-

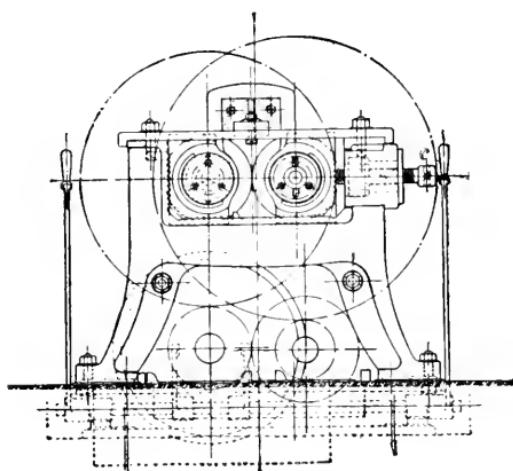


FIG. 11 B.—Mixing Machine, end view

engagement in case of accident. Mills actuated by direct electric drive, which is undoubtedly the most suitable method in large works, are provided with push buttons fitted on various parts of the machine, workable by either hand or foot of the operator.

The first operation in mixing is that of "breaking down," *i.e.* reducing to a plastic condition, the rubber. With a view to saving time this operation, in most large works, is carried out on a separate pair of rolls. The rubber is passed repeatedly through the heated rolls and the latter are gradually tightened up until the rubber is in a thoroughly

plastic—but *not sticky*—condition. It is then transferred to the mixer proper, and the sulphur, minerals, etc., are gradually worked in. The aim of the mixer is to obtain as homogeneous a “dough” as possible. This is accomplished by scattering a part of the sulphur and fillers (in a finely powdered state) over the sheet of plastic rubber travelling round and round the front roll, cutting or tearing the sheet away, folding and refolding, again working on the rolls, scattering on more of the fillers, and so on, until the non-rubber is distributed as evenly as possible. The operation of mixing requires considerable experience, particularly in regard to the length of working and the temperature of the rolls. Rubbers that are inclined to be soft and sticky must be worked at a much lower heat than hard, nervy rubbers, and it is also essential that the rubber should not be over-worked. As a general rule it may be said that if there is any doubt as to whether a mixing should be run at a higher heat or for a longer period, it is better to run at a lower heat

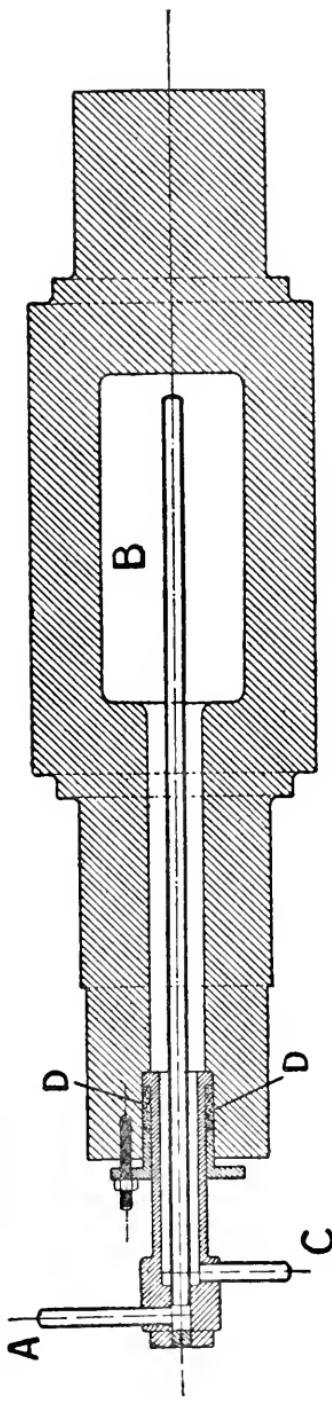


FIG. 12.—Method of Heating Mixing Rolls (see p. 191)

(Steam or cold water are admitted at A, travel into hollow chamber of roll B and out at C. The gland is packed as indicated at D)

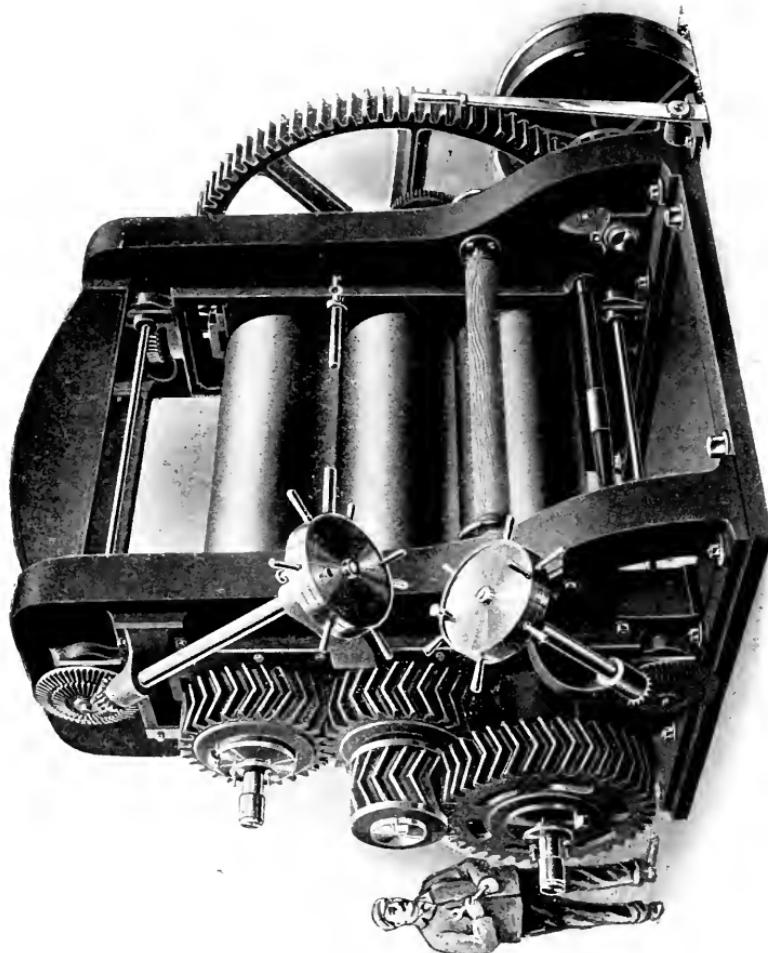
and to lengthen the period of working than the reverse. The essential points in connexion with mixing are that the dough must be obtained in as homogeneous a state as possible, subject to the rubber not being rendered sticky or overworked.

Although many attempts have been made to replace the apparently crude method of mixing by a more scientific process, all such attempts have, as far as I am aware, failed. The first thing that occurs to one is that the rubber might be made into a thin paste with a solvent, the sulphur added in a dissolved form, and the solid matters then admixed. This, however, means considerable cost for solvent, and, in addition, the removal of the latter. If this were all, however, it is possible that some process based on these lines might find a place in the industry, but, unfortunately, rubber which has been treated with a (rubber) solvent always appears to lose strength very badly.

The question of the mechanical working of rubber is one which is well worth exhaustive investigation. We have already seen that it is possible, if the crude rubber is properly prepared, to do away with the washing process; if means were found to avoid the mechanical working of the mixing process as well, another very great step forward would be gained. In this direction it is interesting to note the suggestion of Mr. Kelway Bamber, who proposed to incorporate the sulphur and other matters with the latex or during the process of coagulation, thus avoiding all mechanical working. I am not aware that this process has been tried on a technical scale, but certainly it is difficult to see at present how it would be possible to apply it except under very special circumstances. Nevertheless, it is a suggestion in the right direction.

#### CALENDERING

The primary object of calendering is to transform the rubber dough into sheet form, and it is from calendered sheet that the vast majority of rubber articles are made.



THREE-WHEEL CALENDAR, FOR FRICTION AND EVEN SPEEDS  
(SEE P. 166)



Fig. 13 illustrates diagrammatically the method of operating a calender. The rubber dough R is fed between A and B, and is converted by these very massive and truly turned

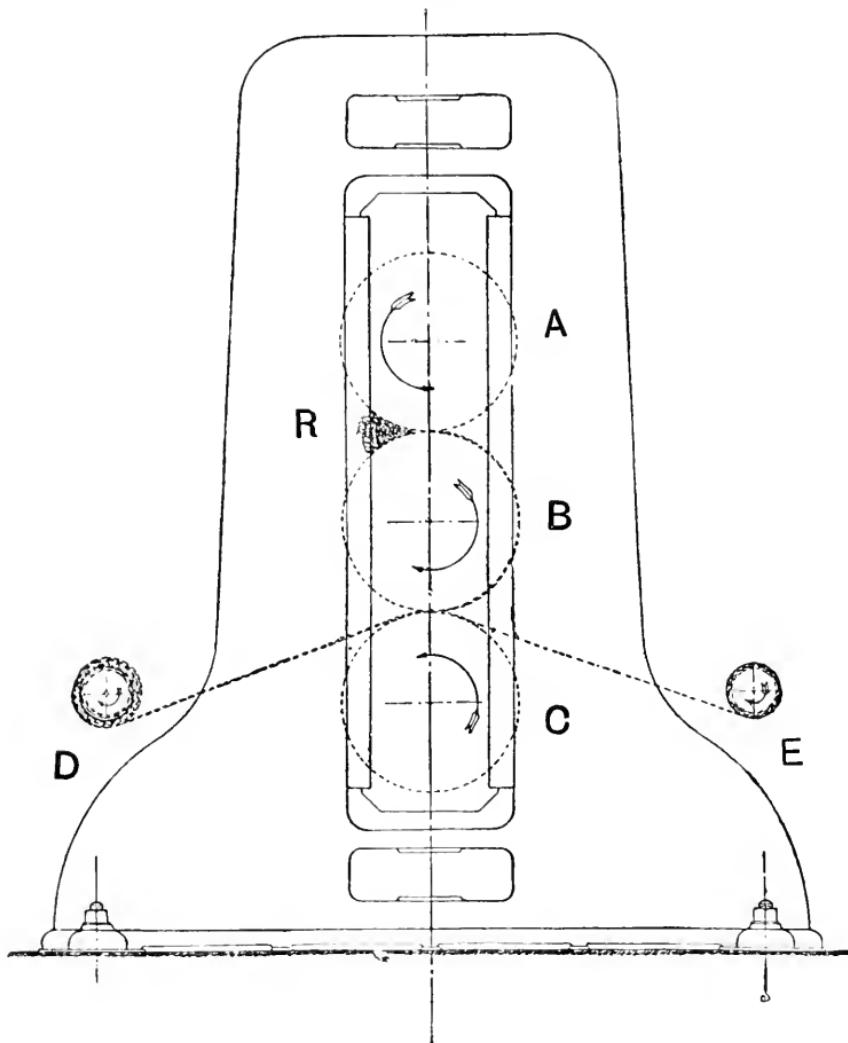


FIG. 13.—Diagrammatic sketch of Rubber "Dough" passing Three-Bowl Calender

rolls into a homogeneous sheet, which is then evenly distributed by the action of rolls B and C on a coarse cloth travelling from a roller E through B and C, and then wound

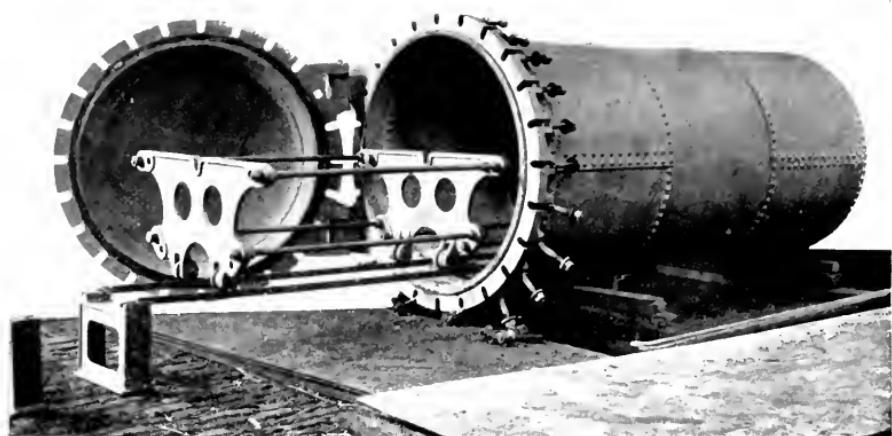
upon D. The dough is calendered on to cloth in order to prevent the layers of rubber dough from sticking to one another. There are two main types of calender, the ordinary even speed calender for producing sheet such as that described above, and the friction calender, which is employed for frictioning or spreading very thin layers of rubber on textiles for waterproofing or other purposes. The principle of the friction calender is the same as that of the ordinary machine, the only difference being that the rolls move at differential speeds, with a view to getting the maximum spreading effect. In many works calenders fitted for both even and friction speeds and with the necessary change gear are employed, as the calender is a costly piece of machinery and is best kept fully occupied. Plate XXIX. shows a modern calender of this type made by Messrs. David Bridge & Co. This illustration will also serve to indicate the extremely massive character of the calender, the method of setting the rolls, etc.

#### “MAKING-UP”

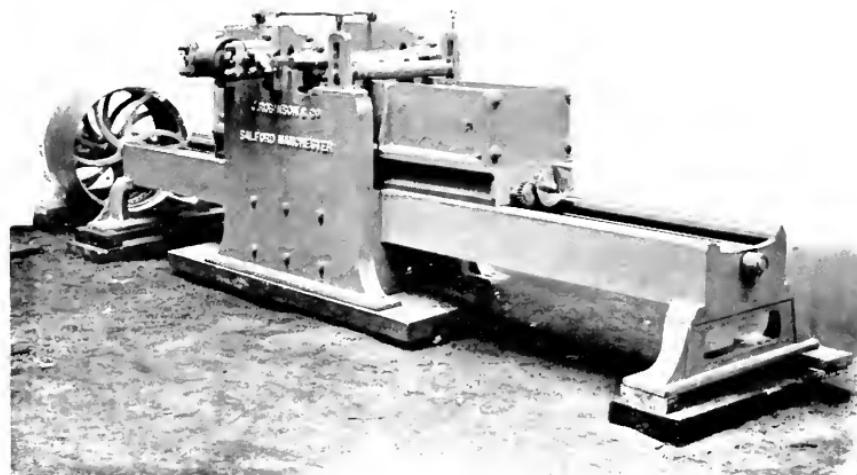
Before the calendered sheet can be vulcanized it must be ‘made-up’ into sheets, strips, discs, etc., of appropriate size and thickness for the intended purpose. If sheet is to be made it is only necessary to cut<sup>1</sup> the calendered material to the desired size and to superimpose a number of layers until the thickness desired is obtained. Washers, heels, valves, and similar articles are generally stamped or cut from calendered sheet by mechanical contrivances and then vulcanized in moulds. In the case of tyres, hose, and similar goods, the making-up is a more complicated process, and requires much skill. Special goods of this kind will be referred to below.

<sup>1</sup> This work is done by hand, a wet knife being employed.





A  
LIVE STEAM ("OPEN-CURE") VULCANIZER  
(SEE P. 100)



B  
FLAT SHEET CUTTING MACHINE  
(SEE P. 207)

## VULCANIZING

*Hot Process*

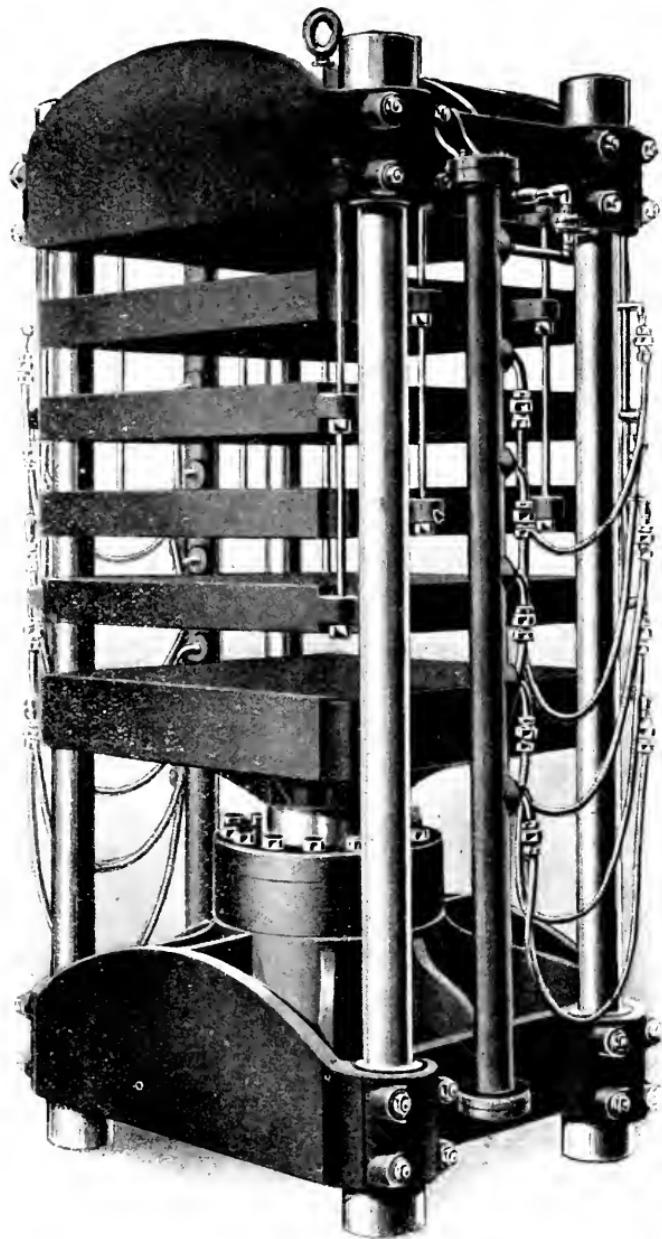
Broadly speaking, the processes employed in *hot* vulcanization may be divided into two classes, namely, those in which live steam is employed, and those in which the heat is directly or indirectly derived from some other source. Opinions still differ regarding the relative merits of the various types of processes—I refer, of course, only to those cases in which alternative methods are practicable—but I am inclined to view with much sympathy the contention that where live steam can be employed, this method gives the most favourable results. I think there can be no doubt that live steam has some specific action, and that it is, compared with other methods, not only a question of even distribution of heat and ready control of temperature. That this is the case is clearly proved by the fact that many mixings containing no "catalyst" (such as litharge or magnesia), which are readily and thoroughly cured in live steam in, say, two hours, at 45 lb. pressure, remain under-vulcanized if press-cured under as nearly as possible the same conditions of temperature, even after six to eight hours. That the even distribution and control of heat which is a feature of the live steam cure is an immense advantage, cannot be denied, and if, as apparently is the case, there has been a tendency to replace the live steam cure by vulcanization in steam-jacketed vessels or by the hydraulic vulcanizing press, this is due to practical considerations of a specific rather than of a general character. For instance, mixings containing oil "substitutes" to any considerable extent do not give the best results in live steam, on account of the saponifying action of this medium at vulcanization temperatures. Again, considerable time is consumed in blowing off steam from a "live" vulcanizer, and there is therefore a saving in this regard where a jacketed vessel or a press is used. If steam is let off rapidly the goods

show a tendency to porosity. In the manufacture of such articles as goloshes, live steam is, of course, out of the question, as it entirely spoils the surface of the goods.

### *Press Curing*

Although temperature and the method of applying heat are the most important factors in vulcanizing, there is a second important factor, namely, *pressure*. If it were advisable to enunciate any hard and fast maxim regarding vulcanization, I should say that given the appropriate heat conditions, the greater the pressure to which the article is subjected, the better the result. It is for this reason that many articles which were formerly cured "in the open" or in moulds are now cured in the press. The main advantages of the press are—(1) That the even distribution of pressure permits of the manufacture of relatively large articles of a homogeneous character—for instance sheet; (2) that in the case of many moulded goods it affords a convenient and economical method of applying an even pressure, capital being thereby saved in regard to cost of moulds, etc.; (3) that a following pressure can be applied and that the pressure can be regulated independently of the heat. The press cure, like the hot air or steam jacket cure, can, of course, also be applied to mixings containing ingredients liable to attack by steam.

A disadvantage of the ordinary hydraulic vulcanizing press is that it is extremely difficult to control the temperature of the plates to a nicety. Owing to steam condensation in the interior and radiation of heat from the exterior of the hollow plates, it is by no means an easy task to keep the plates at exactly the required temperature, or to maintain an even temperature on both sides of the goods in the press. It will be readily seen, also, that the edges of a sheet or the exterior of a mould, for instance, will be exposed to different heat conditions from those obtaining in the central or interior parts of the object under pressure.



HYDRAULIC VULCANIZING PRESS  
(D. BRIDGE AND CO.)



*The Autoclave Press*

Of late years there has been an increasing tendency to combine the advantages of the press with those accruing from the live steam cure; this is accomplished by means of the jacketed or autoclave press. In principle this consists of a hydraulic press, the working parts of which are enclosed in an air-tight chamber, to which steam is admitted in much the same way as in the ordinary live-cure vulcanizer.

Various processes of vulcanization are illustrated on Plates XXX.*A*-XXXII. Plate XXX.*A* shows an "open-cure" (live steam) vulcanizer made by Messrs. J. Robinson & Co. Vulcanizers of this type are made up to a very large size, 70 to 80 feet in length by 4 to 6 feet in diameter not being uncommon. For cable and hose work even larger vessels are made. A very similar type of vulcanizer is made with a steam-jacket, the object being to get the vulcanizer well heated before admitting steam to the interior, thus avoiding excessive condensation. The trays containing the goods are placed on the carriage, and the latter is run into the interior by means of the rails. Needless to say, vulcanizers of this type are (or should be) fitted with all the necessary gauges, thermometers, etc. It is a good plan to have gauges and thermometers of the recording type, and in some works the excellent plan of having a set of indicating and recording instruments (connected with the vulcanizer in a suitable manner) in the works manager's office, is adopted. Plate XXXI. shows a small vulcanizing press of modern type (this particular press is designed for heels and small mould work) made by Messrs. D. Bridge & Co. The pressure is applied by means of a hydraulic ram, as indicated. The hollow plates are connected up with the main steam supply by means of flexible connexions, to allow of free movement of the plates. Presses of this kind are, for the manufacture of sheet and driving belts, made up to a very large size. Plate XXXII.*A* illustrates one of Messrs. Robinson's autoclave presses and

*B* is a jacketed press specially made for vulcanizing tyre covers.<sup>1</sup>

Another method of hot vulcanization which is now used on a somewhat extensive scale is the Waddington dry heat process. This is largely employed for vulcanizing proofed textiles which were formerly cold cured. It consists, in principle, in passing the cloth on which a skin of rubber dough has been frictioned or spread, over a series of rollers contained in a closed stove or chamber. The time of passage and heat are so regulated, that as the textile emerges from the chamber it is just cured to the proper point.<sup>2</sup>

#### *Cold Vulcanization*

The method of vulcanizing rubber in thin layers by means of a dilute solution of sulphur chloride ( $S_2Cl_2$ ) was discovered by Parkes in 1846. The diluent most generally employed for the active agent is carbon bisulphide. The strength will vary according to the article and purpose for which it is intended, but, roughly speaking, 2 per cent. to 3 per cent. are the most ordinary working strengths. The theory of cold vulcanization has been discussed and need not, therefore, be referred to again, and it would be beyond the scope of this work to deal in any way exhaustively with the cold curing process, inasmuch as that would involve a detailed discussion of the methods of the proofing industry, of the manufacture of tobacco pouches, etc. The barest outline of cold curing must therefore suffice.

#### *Spreading*

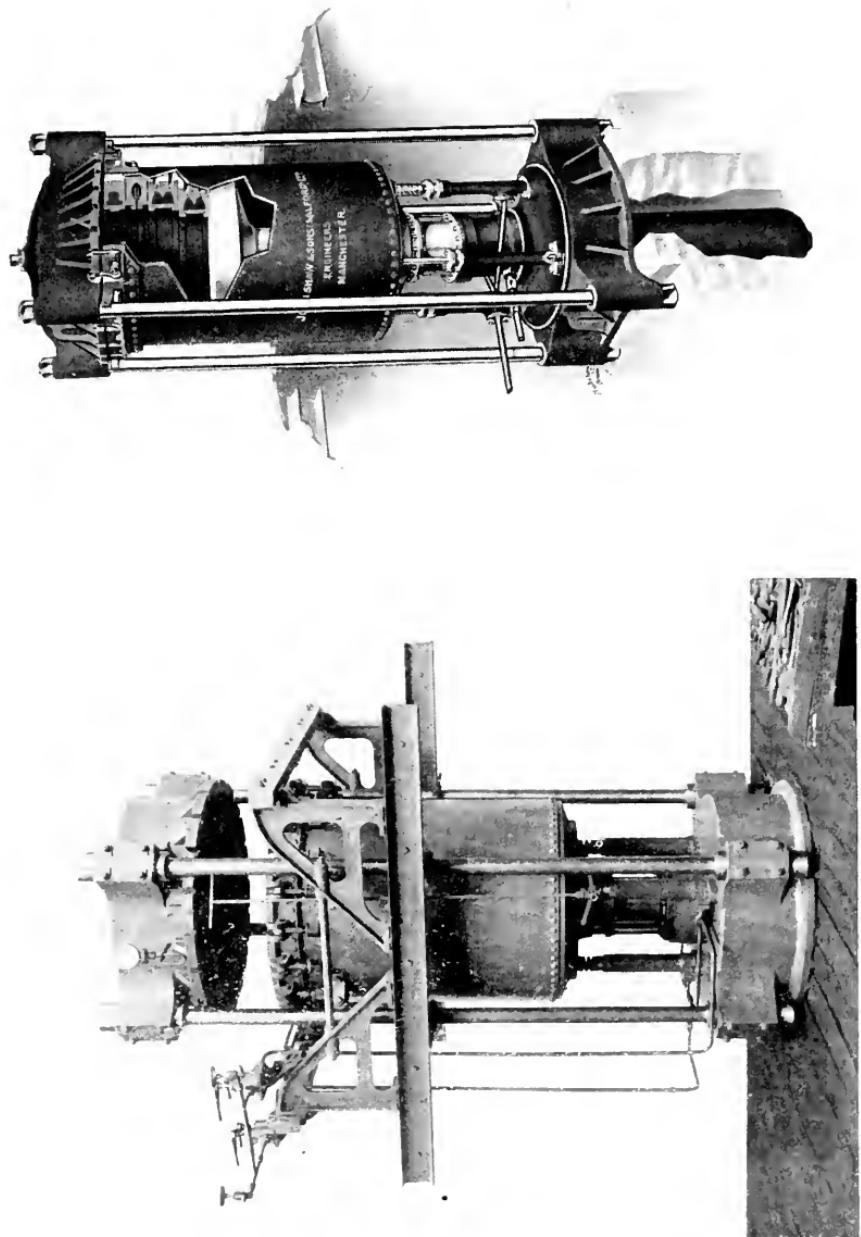
The bulk of the cold-cured articles produced belong to the proofing industry. The first operation in the manu-

<sup>1</sup> For details concerning the construction of autoclave presses of various types, cf. *G.Z.*, 1911, vol. xxv. p. 565 and p. 599. For general details of vulcanizing apparatus and methods, cf. Heil and Esch, *The Manufacture of Rubber Goods* (C. Griffin & Co., London, 1909), pp. 59 *et seq.*

<sup>2</sup> I may add that certain articles (for instance teats) are vulcanized by dipping into molten sulphur.

AUTOCLAVE TYRE PRESS  
(SEE p. 199)

I. ROBINSON'S HYDRAULIC AUTOCLAVE VULCANIZING PRESS  
(SEE p. 199)





facture of proofed textiles consists in spreading a very thin layer of rubber as evenly as possible over the fabric. This process is repeated until a coat of sufficient thickness is obtained. This operation is performed by means of a spreading machine such as is shown on Plate XXXIII. A diagrammatic representation of a spreader is shown in Fig. 14. The spreading machine is a long iron steam-chest, which is fitted at one end with a horizontal roller, above which there is an adjustable iron "doctor." The cloth which is to be treated passes between the roller and the gauge, a thin layer of paste (made of rubber "let down" with a solvent), regulated by the gauge being applied to the cloth during

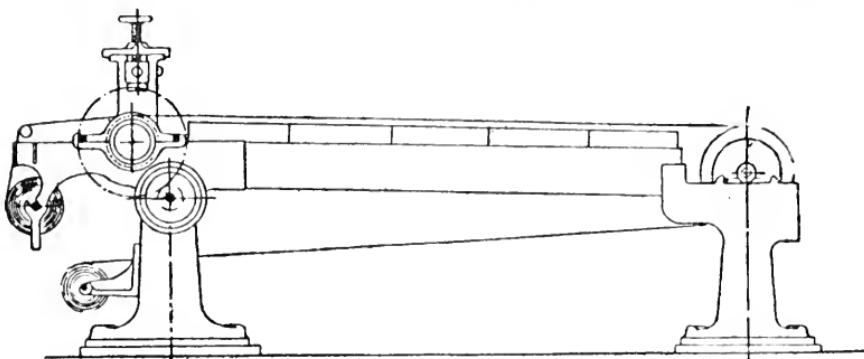


FIG. 14.—Diagrammatic representation of Spreading Machine

its passage. The cloth then passes along the steam-chest, which serves to evaporate the solvent. This operation is repeated until the number of coatings desired has been applied. Spreading involves the use of a good deal of solvent, and for the purpose of recovery, hoods communicating with refrigerating plants are occasionally fitted. In view of the loss of solvent, the tendency of late years has been to replace the spreader by the friction calender wherever possible. Although the calender is more economical in working, there is some difficulty in obtaining an even proofing with it, particularly when only a very thin layer is required.

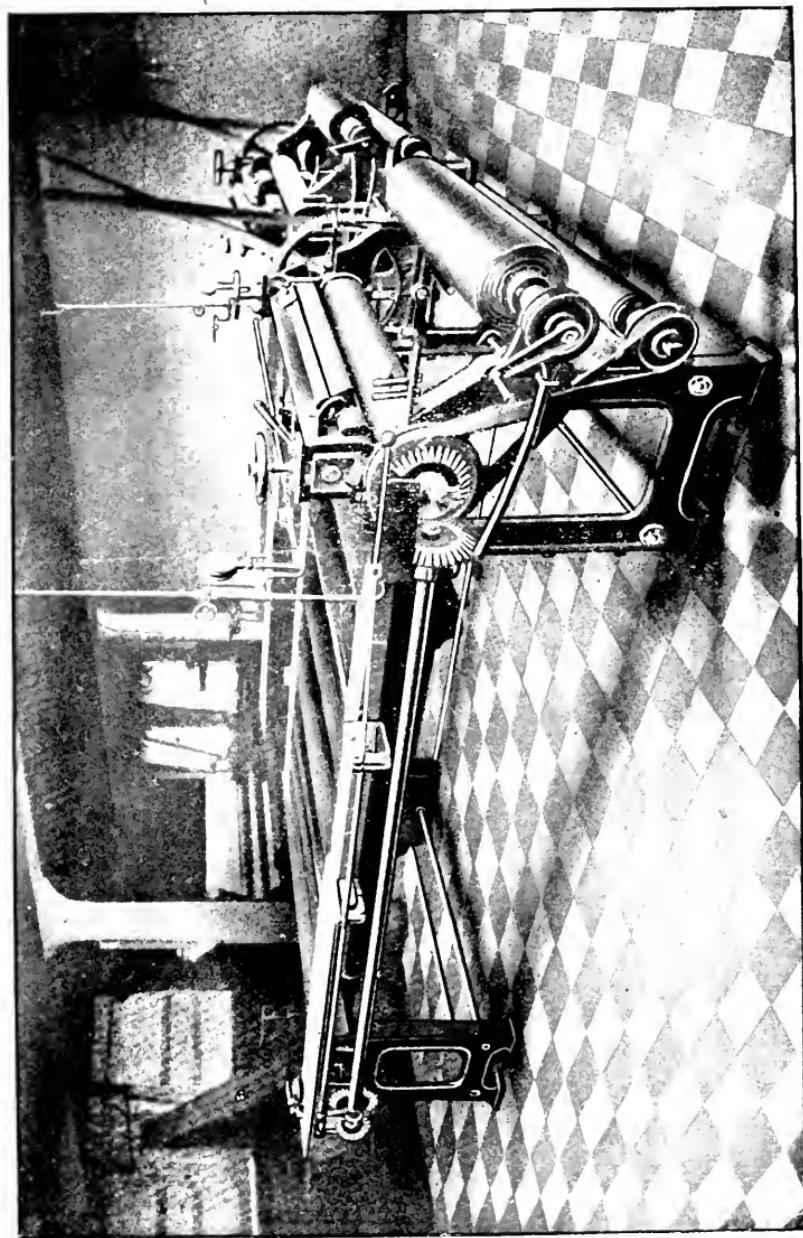
The process of "cold-curing" is, in principle, simple,

but in practice, like many other technical operations, requires considerable experience and knowledge of detail. Substantially it consists in dipping the articles to be vulcanized in, or passing them slowly through, a trough containing the sulphur chloride dissolved in carbon bisulphide. Those who have some working acquaintance with technical operations will readily perceive the difficulties connected with the application of the poisonous and inflammable materials used, with the removal of the excess of the solvent, with the—in view of the powerful nature of the reagent employed—prevention of over- or under-vulcanization, etc., but it is beyond the scope of this book to enter into these matters more fully.<sup>1</sup> "Proofing" is a highly specialized industry, and in this respect may be compared to another branch of rubber manufacture, namely, cable making. It involves such problems as the selection and preparation of suitable basis materials (cotton, silk), the application of dyes, pigments and lustres, the "finish" of the goods with shot, highly glossy and matte effects, the manufacture of "single" and "double" textures, and so on.

#### *Conditions affecting Vulcanization*

*Nature of the "mixing."*—The specific purposes for which various ingredients are employed have been referred to in general terms, but in summarizing the conditions affecting vulcanization, it is, I think, desirable to point out that each case which arises in practice must be considered on its own merits, and in the light of the particular purpose for which the article to be manufactured is intended. Very broadly speaking, there is an optimum of the main vulcanizing conditions (time and temperature) for each mixing, and if some modification of the properties of the finished article is required, it is therefore better to alter the mixing rather than the vulcanizing conditions. For instance, if goods of a relatively hard character are required, it is not advisable to try and attain this object by over-vulcanizing. Naturally,

<sup>1</sup> Cf. Heil and Esch, *op. cit.*



SPREADING MACHINE

(D. BRIDGE AND CO.)

(S.P.E. P. 291)



I refer here only to goods requiring the same general style of vulcanization.

In considering the character of the finished product, it must be borne in mind that a more or less considerable after-vulcanization takes place, and this tends to stiffen or harden the goods. *Cæteris paribus*, the more free sulphur present in the freshly vulcanized goods, the greater this effect will be. Correctly vulcanized soft articles are, as a rule, not at their best until a month or two after manufacture has elapsed. Goods which are practically perfect when fresh, almost invariably show signs of over-curing after a few weeks or even days. A very fair idea of the deterioration likely to take place in this connexion may be obtained by subjecting the goods to a dry heat ( $60^{\circ}$  to  $70^{\circ}$ ) in a thermostat, and examining them at intervals of twenty-four hours. In certain classes of goods, *e.g.* cables, it is highly important that after-vulcanization should be reduced to a minimum, and this result can only be attained by perfect vulcanization under conditions which leave a minimum of sulphur in the material.

The various methods of vulcanization have been referred to in some detail, and need not be repeated, but it may not be superfluous to indicate that if a specific desired result cannot be attained by altering the nature of a mixing—assuming that the optima of time and temperature have been found—the remedy may lie in substituting, say, the autoclave press for the open press, or hot air for live steam; or, again, in moulding the goods instead of wrapping, etc.

*Time of Cure and Temperature.*—It has been found in practice that a slow rise of temperature is necessary, in the majority of cases, to obtain the best results. For instance, in press-curing, a standard method for sheet, say, a quarter of an inch thick, is a slow rise of half an hour to three-quarters of an hour up to a steam pressure of 45 lb. (=roughly to a temperature of  $135^{\circ}\text{C}$ . ( $275^{\circ}\text{F}.$ ) and 3 atmospheres), with a subsequent period of one and a half to two and a half hours at this pressure. The known facts

regarding the "slow rise," viewed in the light of Axelrod's theory<sup>1</sup> concerning the vulcanization process, and more particularly of the formation of the "kinks" on the vulcanization curve, suggest that the adsorption of sulphur up to the point at which chemical action starts, is a relatively slow process, and that rapid heating causes an excessive increase in the ratio  $\frac{\text{disaggregation}}{\text{adsorption}}$ . The views expressed above may, at first sight, appear to be in conflict with the results obtained by the Doughty process of quick vulcanizing.<sup>2</sup> This is stated to consist in heating the goods—in the case of cycle-tyre covers—for three minutes to a temperature of  $187^{\circ}.7$  ( $370^{\circ}$  F.), and to answer perfectly for relatively thin articles. In this case, however, we are dealing with a set of conditions entirely different from those of ordinary vulcanization, and if Erdmann's views<sup>3</sup> regarding the formation of "thiozonide" at about  $160^{\circ}$  are correct, his hypothesis might well explain the Doughty reaction without conflicting with Axelrod's views or the known facts concerning the "slow rise."

*General Rule.*—The vulcanization effect is increased—

- (a) By prolonging the time of the cure ;
- (b) By raising the temperature ;
- (c) By increasing the quantity of vulcanizing materials.

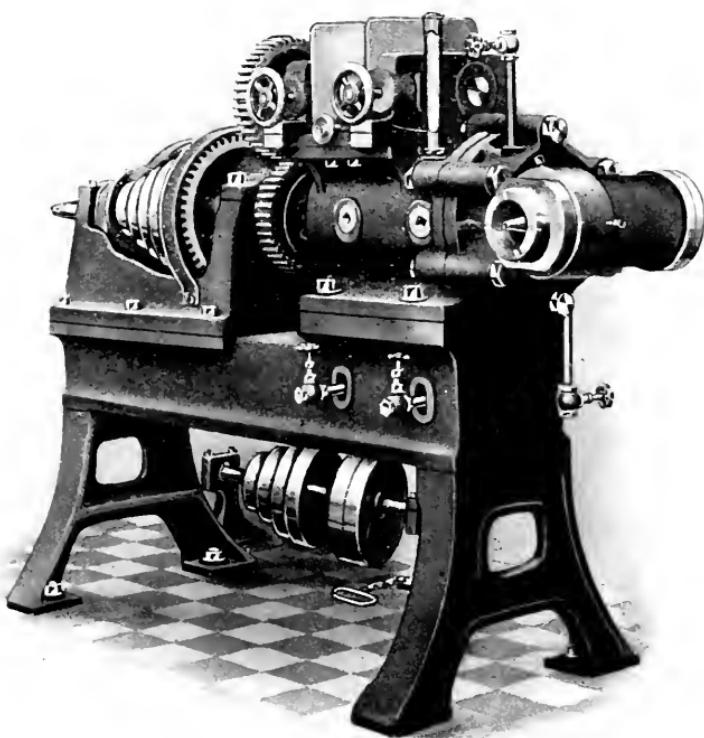
The question may arise in practice: Which of these factors must be modified to achieve a specific effect? This question may be broadly answered as follows: (a) Where it is desired to produce a relatively hard article,<sup>4</sup> it is better to increase the quantity of the sulphur or other vulcanizing

<sup>1</sup> Cf. p. 167.

<sup>2</sup> Cf. Terry, *India-Rubber and its Manufacture*, 1907, p. 89 (London: Constable).

<sup>3</sup> Cf. p. 168.

<sup>4</sup> It will be remembered that as vulcanization proceeds, the tensile strength and hardness of the material increase, but that the elasticity, or rather dis-tensibility, decreases.



FORCING MACHINE (FOR "SQUIRTING" CAB TYRES, TUBING,  
CORD, ETC.) WITH ROLLER FEED, HINGED NOSE-PIECE,  
STEAM-HEATING AND WATER-COOLING GEAR

(SEE P. 205)



materials, than to attempt to gain the desired effect by prolonging the cure or raising the heats; (*b*) in making soft goods in which only small quantities of sulphur can be employed, time and temperature are the salient factors, but it is preferable to alter the time of the cure, rather than the heat.

## THE MANUFACTURE OF VARIOUS RUBBER ARTICLES

### *Pneumatic Tyres*

The inner tubes are made up in several ways, but generally from calendered sheet which is cut to the desired shape, placed on a mandrel, and joined together by means of a thin slip of rubber and "solution." Another method is to build up from two pieces, the joint of the one being opposite to that of the other, or, again, calendered strip is wound spirally on the mandrel and then back again in the opposite direction, a perfectly jointless tube being thus obtained. The tube is then wrapped in cloth and vulcanized in the open, and subsequently removed from the mandrel by compressed air or other means. Excellent inner tubes have also been made for some little time past by "forcing." Tyre covers are built up on the mandrel from layers of canvas and calendered sheet. They are vulcanized in batches in iron moulds, preferably in a hydraulic autoclave press (see Plate XXXII.).

### *Solid Tyres*

Are generally "squirted" through an appropriate die in the forcing machine, and vulcanized in lengths in French chalk with live steam. The general principle of the forcing machine may be gathered from Fig. 15. In a recent type of machine, such as that made by Messrs. Bridge, and illustrated by Plate XXXIV., the rubber dough is fed in by a small pair of rolls. This is a distinct improvement over the ordinary hopper feed. The dough on entering the machine is carried forward by means of a screw or

similar device, which ultimately forces it into the nozzle and out through the die. The "forcer" is provided with a steam-jacket in order to maintain the dough in a thoroughly plastic condition, and modern machines are fitted with the necessary devices for accurately controlling the temperature. Special types of solid tyres are also made (either from forced dough or from calendered sheet) in moulds either in the press or in live steam.

### *Cut Sheet*

The manufacture of cut sheet is practically a monopoly (in the United Kingdom) of three or four firms. The

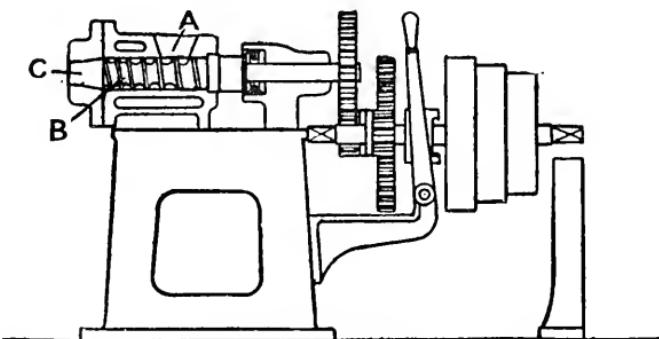
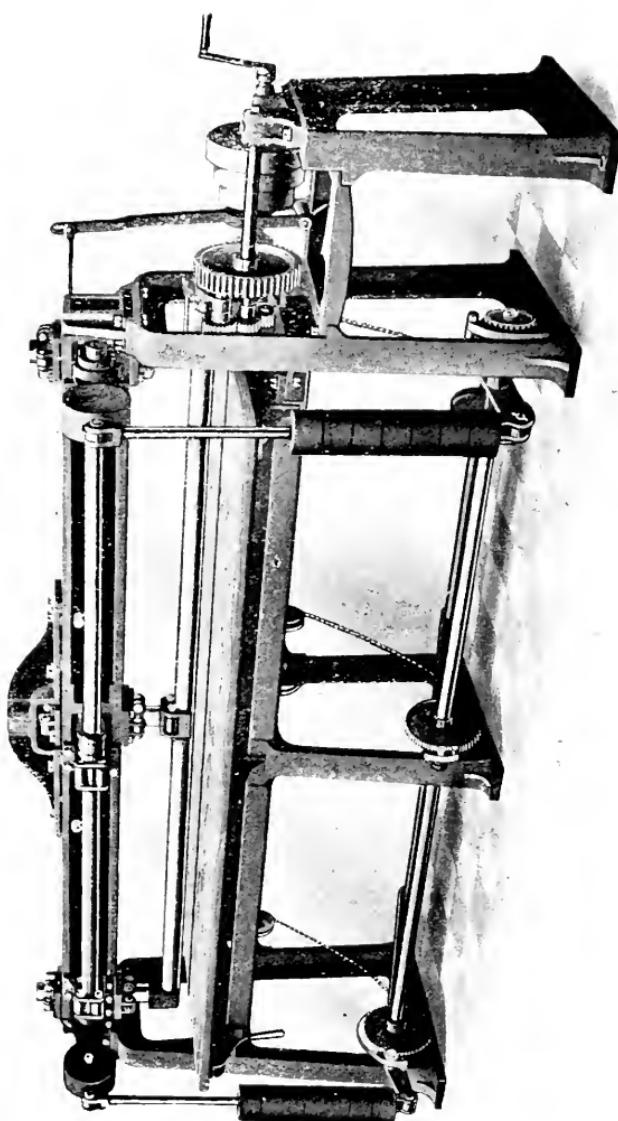


FIG. 15.—Forcing Machine (diagrammatic)

The rubber dough is fed in through hopper A, is carried forward by screw B, and so forced through an appropriate die fitted to nose-piece C.  
(See page 205 and Plate XXXIV.)

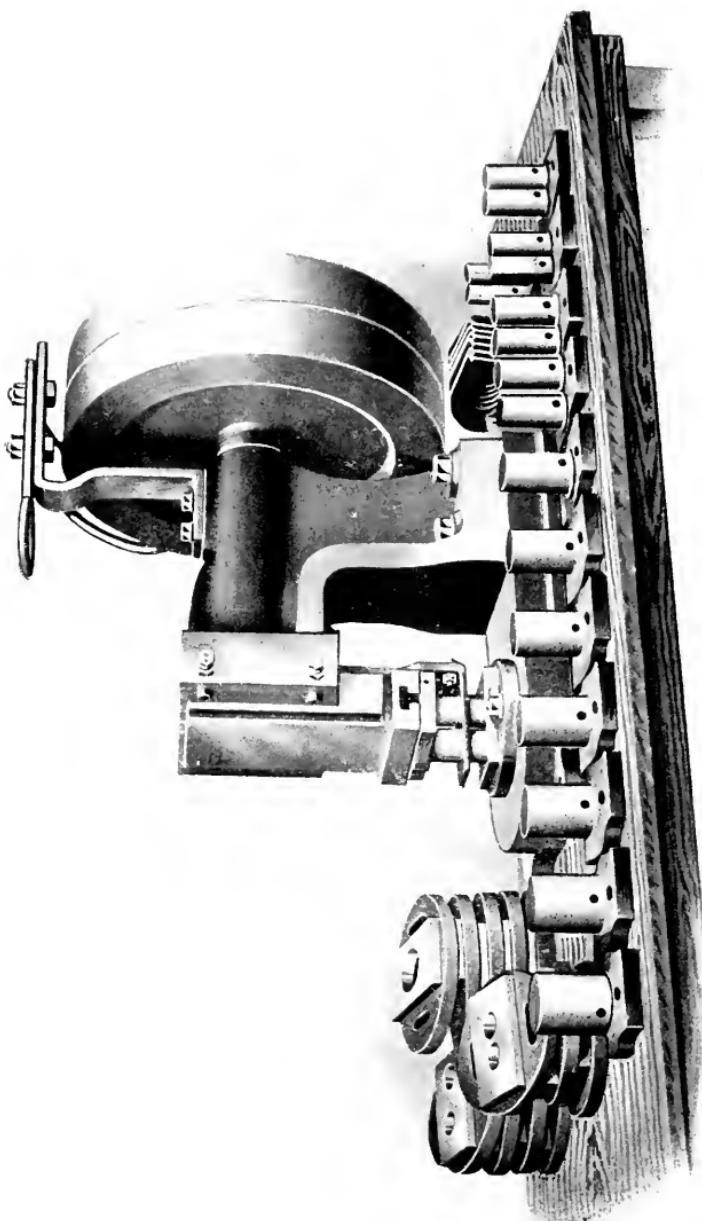
importance of this article, which is used for making thin, very high class goods, such as tobacco pouches, surgical materials, feeding outfits, etc., appears to be gradually diminishing, partly on account of the difficulty and expense of manufacture, partly owing to the improved quality of "rolled" sheet obtainable by modern calender work. The majority of articles made from cut sheet are cold cured, but a few—for instance, feeding teats—are vulcanized by immersion in a sulphur bath. The method of making cut sheet is broadly as follows: The rubber is thoroughly masticated in a special type of masticator, and then pressed



WRAPPING MACHINE  
(SEE P. 217)







STAMPING MACHINE AND DIES  
(FOR MAKING RUBBER HEELS, ETC.)

into cylinders or blocks. Subsequently, it is forced out of the pressure vessels and frozen. In former times the blocks were frozen by placing them in a freezing mixture of ice and salt, but in modern plants refrigerating machinery is employed. The frozen rubber is then cut into thin sheets by means of rapidly moving knives. A cutting machine for making sheets from square or rectangular blocks is shown in Plate XXX.B. The carriage travels backwards and forwards, and after the cutting off of a sheet, the block is raised through a height equal to the thickness of the sheet. Another type of machine is designed with a view to cutting an endless length of sheet from a cylindrical block. The adjustment and working of the knives, and the movement of the block so as to secure even cutting, are matters involving very great technical difficulties. In recent years "mastication" has been largely replaced by merely cutting the rubber into small pieces and then subsequently pressing, the "working" of the rubber thus being avoided.

### *Elastic Thread*

This material is largely employed for all kinds of elastic "webbings," such as those used in the manufacture of braces, garter material, "side-spring" boots—now almost a thing of the past—for winding the cores of golf balls, etc. Elastic thread, like cut sheet, is made by a very limited number of firms, and at one time its manufacture was practically a British monopoly. The process of manufacture is, briefly, as follows: The rubber is masticated with a certain quantity of solvent naptha and sulphur, and is then frictioned on to cloth. It is then removed from the cloth and wound round an iron drum (interlined with cloth) and vulcanized in open steam. After vulcanization it is removed from the iron cylinder, pasted over with shellac and wound on to a roller. It is then cut on the latter to the requisite size, and subsequently boiled with caustic soda to remove the free sulphur and shellac. This is very necessary, for otherwise a rapid hardening of the goods takes place.

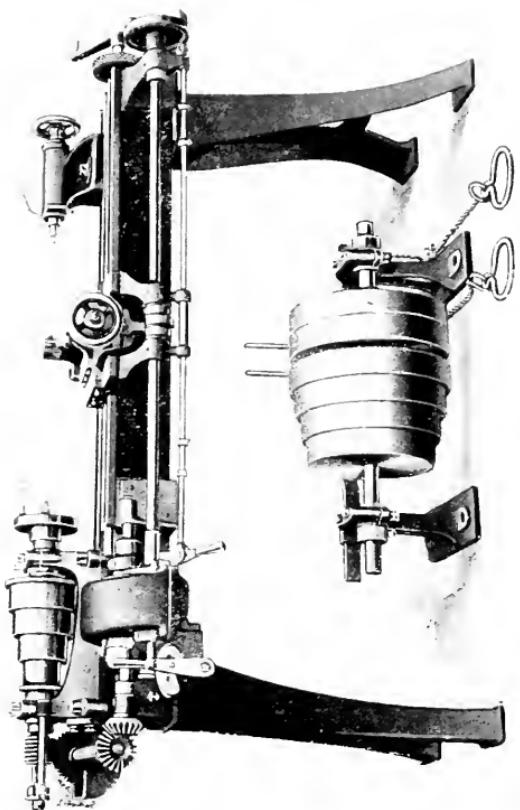
*Rubber Hose*

Different types are made up from calendered sheet or seamless (forced) tube and proofed fabrics—canvas, etc.—with or without metallic strengthening insertions. Most kinds of hose are made in considerable lengths (60 feet is a standard size), and practically all the operations are performed by machine. A long mandrel, horizontally disposed in a wrapping machine (see Plate XXXV.), is wrapped with alternate layers of rubber and canvas. The length is then bound with canvas, and the whole vulcanized in a layer of French chalk in open steam. If a seamless inner tube is used, this is drawn over the mandrel, and the necessary layers of canvas, etc., are then wrapped on. In some kinds of hose the seamless tube is not covered with canvas on the ordinary horizontal type of wrapping machine, but is drawn simultaneously with a canvas strip through an apparatus which folds the latter over the tube. Occasionally, instead of wrapping with canvas, the yarn is spun directly on to the lapped sheet or tube. Vacuum hose and other types of suction hose (*e.g.* that for mining work) are formed round an inner core of spirally wound wire. Railway vacuum hose is made up in short lengths by hand. Garden hose is simply squirted tube made from a rather low grade mixing.

*Rubber mats* are pressed or moulded from calendered or roller sheet, the pattern being given either by pressing or moulding.

*Rubber heels and heel pads* are stamped from sheet and subsequently vulcanized in moulds. A stamping machine for cutting out rubber heels and similar articles, together with types of moulds employed, are shown on Plate XXXVI.

*Buffer springs, washers, etc.*, are made by lapping calendered sheet round a mandrel until a cylinder of the requisite size is obtained. In certain cases the articles are cut from the cylinder before vulcanization, and are then separately vulcanized in moulds. In other cases the whole cylinder is vulcanized and the articles are cut off afterwards.



MACHINE FOR CUTTING RINGS, DISCS, ETC.



Washers, valves, and rings are also made by cutting the requisite pattern out of rolled sheet.

*Rubber belting* is made by frictioning dough on to proofed fabric, cutting to the requisite width, and then building up to the desired thickness.

*Rubber sponges*.—The porous effect is stated to be obtained by vulcanizing, under appropriate conditions, a mixing which contains ammonium carbonate or some other material, which becomes volatile at vulcanizing temperatures, so leavening the whole mass in much the same way as baking powder does a flour dough. This sounds simple enough, but, as a matter of fact, the manufacture of rubber sponges is a very difficult branch of manufacture, and successful sponge-making appears to be almost a monopoly of a few Russian and American works.

*Rubber rings*.—According to thickness, these are made by solutioning together rubber tape or cord, or by cutting them from a rubber tube in the lathe (see Plate XXXVII.). Stamping is rarely resorted to. Articles such as *hot-water bottles* and other similar goods are built up by joining pieces cut to the appropriate size and shape with "solution," evaporating the solvent, and subsequently vulcanizing.

## CHAPTER XIII

### SUBSTITUTES AND WASTE RUBBER DISPOSAL

#### SUBSTITUTES

ALTHOUGH in the proper sense of the term no substitute for rubber exists, there is a special class of substances which are known as "substitutes" in the industry. These materials are produced by vulcanizing vegetable oils, such as colza, rape, maize, and cotton-seed oils either in the cold with sulphur chloride, or hot with sulphur. Substitutes produced by the cold process are generally known as white substitute, those by the hot process as brown or French substitute. They have been produced on a considerable scale for certainly forty years, and a goodly number of patents have been taken out in connexion with their manufacture. As the price of these substitutes varies from about 3½d. to 9d. per lb., it is scarcely necessary to say that their use effects a considerable saving in the cost of the rubber article in which they are incorporated. Broadly speaking, they are employed in order to cheapen the cost of production in cases in which a low price is essential, and where the goods to be produced are to be of low specific gravity. In a cheap mixing in which the gravity is to be kept down, the use of a certain amount of "substitute" counteracts the weight of the mineral fillers. The advantage of the "substitute" over mineral fillers is that the plasticity of the mixing is not affected to any extent, although the strength, wearing qualities, and

elasticity are naturally much influenced. According to Weber, white "substitute" (which is the more expensive) is generally employed only for cold cured goods, but the brown may be employed for either. This, however, is not in accordance with the opinions of some manufacturers of great experience with whom I have discussed this matter, their view being that the white "sub" is the more suitable article for the hot cure. Many other substitutes have been suggested, and some are used on a considerable scale in the place of rubber, particularly in cable mixings. Gums, bitumen, vulcanized bitumen, nitrated oils, nitrated celluloses, ceresine, etc. etc., all find their sphere of utility in cable mixings, in insulating materials, valve rings, and so on, but a true rubber substitute has yet to make its appearance, and the majority of the materials mentioned are used merely as cheapeners or in order to achieve some specific effect (see p. 188).

#### WASTE RUBBER

An enormous quantity of waste rubber finds its way from one source or another into the market. If we assume that the crude rubber employed in the manufacture of goods in the British market yearly amounts to 12,000 tons, and that this reappears in the shape of finished rubber articles, containing on the average perhaps not more than 30 per cent. of rubber, it is plain that there must be something like 30,000 to 40,000 tons of waste rubber annually. Of this, perhaps, one-half is recoverable, the remainder actual waste. The waste rubber industry is an important one in itself, and a special organization exists for the collection of this material. Broadly speaking, waste rubber is utilized in one of three ways: (*a*) It is ground up (where the article permits of such simple treatment) and used direct in the ground state by the rubber manufacturer in his mixings for the cheaper varieties of goods; (*b*) it is subjected to one of the reclaiming processes, which substantially consist in freeing the rubber from fibre, dirt, and particles of metal, and

subsequently removing as much as possible of the free sulphur and non-rubber substances; and (*c*) the rubber is submitted to a reforming process, by *reforming* being understood a process which employs substantially only heat and pressure.

### RECLAIMED RUBBER

In the older reclaiming processes the rubber was simply ground, the metal particles and vegetable fibres removed, and the mass then heated together with mineral oil in stoves, and subsequently rolled out into homogeneous sheets. By this process no sulphur was removed. The newer processes mostly involve wet treatment and the removal of free sulphur, and it must be admitted that some of the reclaimed rubbers so made are of remarkably good quality. Indeed, the better varieties, which are, it need scarcely be said, made from the best qualities of scrap, fetch appreciably higher prices than some of the inferior crude rubbers. The oldest of the wet processes is the acid process, in which fibre is destroyed by means of sulphuric or hydrochloric acid, part of the mineral matter also being removed. The process is chiefly suitable for lightly cured scrap, such as that from proofed goods, as very little sulphur is taken out. In the alkali process, originally developed on a large scale by A. H. Marks, of the Diamond Company, Akron, Ohio, which is employed in some of the largest reclaiming works in the United States and the United Kingdom, the scrap is first sorted, ground, metallic particles removed by magnetic separation, the ground rubber shaken in perforated trays to get it in an evenly divided state, and subsequently heated under pressure in iron vessels with alkali. It is claimed that in this way the whole of the free sulphur is removed. It is needless to say that after emerging from the pressure vessel the material is subjected to a very careful process of washing. Finally, the rubber is sheeted. Another

process which may be mentioned is that in which neutral sulphites are employed for the removal of sulphur. Finally, it is necessary to note that a number of reclaiming processes have been proposed (some of which are, I think, working) in which, after mechanical cleaning, the whole rubber mass is dissolved in a suitable solvent. These solvents are generally of a neutral character and of high boiling points (petroleum, terpineol, etc.). From the solution so obtained the rubber is precipitated by means of a non-rubber solvent such as alcohol. It has recently been stated that reclaimed rubber from which the whole of the sulphur has been removed is being manufactured, but I have not personally come across any material of this type.<sup>1</sup>

### REFORMED RUBBER

During the past few years a number of patents have been taken out (Gare, Immisch, etc.) for processes which effect the direct production of moulded articles from ground or flaked scrap mainly by means of heat and pressure. Exceedingly good results are obtained in this way, and it is remarkable that this simple method of dealing with "mechanical" scrap was not discovered at an earlier date. The fact remains, however, that particles of vulcanized rubber in the shape of dust or flakes can by pressure and heat be moulded to a homogeneous mass, which, on cooling, is to all intents and purposes indistinguishable from an ordinary moulded article.

<sup>1</sup> In Weber's *Chemistry of India-Rubber* it is stated that reclaimed rubber in a mixing may be recognized by the fact that this article is always made with the addition of an oil, but this no longer holds good.

## CHAPTER XIV

### CHEMICAL, PHYSICAL AND MECHANICAL PROPERTIES OF VULCANIZED RUBBER

**I**N considering the properties of vulcanized rubber, it is essential to remember that it is not—even in the case of an article made from rubber and sulphur only—a chemical entity, and that its attributes vary within the widest limits according to the nature of the mixing and method of vulcanization. It is also necessary to bear in mind the fact that no rubber mixing is absolutely homogeneous. Vulcanized rubbers may be sub-divided according to general type into high, low, and medium grades of soft, medium soft, medium hard, and hard rubbers or ebonite, respectively, but, even with so wide a classification as this, it is impossible to draw in all cases a hard and fast line of demarcation.

#### I. CHEMICAL PROPERTIES

*Derivatives.*—The only known substances which possess even approximately the character of chemically homogeneous substances are the bromine and nitric or nitrous acid derivatives. There is a considerable literature<sup>1</sup> on this subject, principally of an analytical character, and from this it seems fairly clear that the sulphur of vulcanization is contained in the derivatives.

<sup>1</sup> Cf. (Bromide) Budde, *G.Z.*, 1907, vol. xxi. p. 1205; Axelrod, *ibid.*, p. 1229; Hinrichsen, *Chem. Zeit.*, 1909, vol. xxxiii. pp. 735 and 928; Hübener, *ibid.*, pp. 144, 155, 648, and 662; and (Nitrosate) Alexander, *G.Z.*, 1907, vol. xxi. p. 727, etc.

*Effect of Oxygen or Air*

As is well known, vulcanized rubber tends, after a time, to become hard and brittle, particularly if freely exposed to air and light. This result is particularly noticeable in low grade mixings containing much free sulphur, substances of an acid character, or materials (such as chalk or zinc oxide) which have a tendency to attract the traces of free acid present in the atmosphere of most large towns. According to Bing,<sup>1</sup> the hardening of rubber is always accompanied or preceded by the formation of free sulphuric acid, and he was able to confirm the fact noted by Burghardt, Thomson, Weber, and others,<sup>2</sup> that very small quantities of copper or copper salts enormously increase the rate of oxidation. An investigation carried out quite recently, under the direction of Professor Martens, at the Königl. Materialprüfungsamt, Berlin,<sup>3</sup> showed—(a) That specimens of soft rubber preserved *in the dark* at room temperature, whether in dry or moist air, underwent very little change over a considerable period of time; (b) specimens similarly treated at a temperature of about 70° hardened considerably (more rapidly in dry than in moist air), owing to after-vulcanization; (c) specimens treated as under (b), but exposed to *light*, underwent a rapid oxidation, which could be followed by the increase in the “resin” content (acetone extract). It is a remarkable fact—which has long been known in practice—that dry heat is more prejudicial to rubber<sup>4</sup> than moist heat. In view of the fact that vulcanization by dry heat is much slower than in steam, it seems to me that the theories to the effect that dry heat deterioration is due to after-vulcanization must be accepted with a certain amount of reserve. It may be noted that moist heat is—owing to the saponifying action of the

<sup>1</sup> Z.K., 1909, vol. iv. p. 232.

<sup>2</sup> Cf. Hinrichsen and Memmler, *op. cit.*, p. 83.

<sup>3</sup> *Ibid.*, p. 84.

<sup>4</sup> The term “rubber” in this chapter will be used as synonymous with *vulcanized rubber*.

steam—particularly detrimental to mixings containing oil-derived “substitutes.”

### *Effect of Acids, Alkalies, etc.*

High grade soft rubbers are relatively stable towards dilute acids. Strong sulphuric acid, naturally, has a charring, strong nitric acid an oxidizing, effect. Mixings containing substances soluble in acids (*e.g.*  $\text{CaCO}_3$ ,  $\text{ZnO}$ ,  $\text{MgO}$ , etc.) are more or less severely affected, according to the quantity of the soluble substances present in the mixing, the strength of the acids, etc. Towards alkalies, even at relatively high temperatures, high grade and medium rubbers are extremely stable, but mixings containing substances soluble in or modifiable by alkaline media (*e.g.*  $\text{ZnO}$ ,  $\text{Sb}_2\text{S}_5$ , oil substitutes, etc.) will obviously be attacked by them. All oils, but particularly *mineral oils*, owing to their solvent action and capacity for hastening oxidation, invariably have a prejudicial effect on rubber.

Pahl and Heinzerling<sup>1</sup> made an exhaustive examination of the effect of various acids, alkalies, oils, and coal gas on a large number of specially prepared mixings. The results arrived at—which, owing to the inaccessibility of the original publication, I quote from Weber—were as follows:—

“All mixtures containing chalk, fluor-spar, litharge, and zinc oxide are strongly acted upon by sulphuric and acetic acid. The action of these acids always causes a considerable increase in weight, due to the formation of either insoluble or basic salts.

“The destructive action of all oils upon india-rubber is more particularly checked by the addition of litharge and zinc oxide; other inorganic admixtures are much less effective. The mixtures examined . . . are not sufficiently modified by either the alkalies or coal gas to allow any definite conclusions to be drawn. All organic admixtures

<sup>1</sup> *Verhandl. des Vereines zur Förderung des Gewerbeleisses*, 1891, vol. viii. p. 351, and vol. ix. p. 10; *ibid.*, 1892, vol. i. p. 25. Cf. also Weber *The Chemistry of India-Rubber*, p. 162, *et seq.*

protect the compound more or less from the corrosive action of the acids.

"There is a general tendency in india-rubber containing inorganic admixtures to harden and become brittle on prolonged storing. They also offer less resistance to mechanical influences, but their insulating power appears to remain unimpaired."

Broadly speaking, the results obtained by Pahl and Heinzerling confirm my own experience in connexion with the action of chemical agents on rubber mixings; the remainder of their work, which deals with the mechanical properties of a large number of mixings, is, however, open to serious criticism. The methods of determining breaking strain and elongation adopted by them are scarcely of a character to inspire confidence, and, as Weber has pointed out, all the mixings were vulcanized under identical conditions of temperature, pressure, and time. Under these conditions it is practically certain that many of the samples must have been over-, many others under-cured. To obtain reliable vulcanization results it is necessary to test each sample over a range of time and temperature. Moreover, descriptions of the physical and chemical properties of rubbers made with certain mixings are of very little value if it is patent that the process of vulcanization employed was not appropriate. For instance, to determine the tensile strength of rubbers made from a number of different mixings all vulcanized, say, in live steam, may be academically interesting, but they are not necessarily of much practical importance; for it is probable that if these mixings had been cured, say, in the vulcanizing press, they would have shown entirely different results. Particularly is this so when we are aware that in practical manufacture such articles would have been made in the press. It may be said that the results shown by different mixings all vulcanized under the same conditions are, at any rate, comparable, *inter se*, even if the method of vulcanization is not the most appropriate or the best, but I very much doubt whether even this is the case.

## II. PHYSICAL PROPERTIES

The most important *physical* properties of rubber from a practical point of view are its relative stability towards changes of temperature, impermeability to water and gases, and its utility as an electrical insulator. With regard to changes of temperature, we know that ordinary air or room temperatures do not affect vulcanized rubber to any marked extent ; it does not, as is the case with crude rubber, become rigid and hard at winter temperatures, or soft and sticky at many degrees below the boiling point of water. At the same time, we have seen that it is to some extent affected by a moderate heat (say 50° to 70°) if exposed for any length of time, and this effect is very pronounced in the case of low grade mixings. Well vulcanized rubbers prepared with suitable mixings absorb very little water under ordinary conditions, but under heavy pressures, such, for instance, as obtain in deep-sea cable work, it is by no means impermeable, and in this respect is decidedly inferior to gutta-percha. As a matter of fact, rubber is scarcely used at all for marine cables, mainly on this account.

### *Permeability to Gases*

Graham<sup>1</sup> measured the rate of diffusion of various gases through rubber membranes, with the following results, taking the rate of diffusion of nitrogen = 1. :—

Nitrogen . . . . .	1,000
Carbon monoxide . . . . .	1,113
Air . . . . .	1,149
Methane . . . . .	2,148
Oxygen . . . . .	2,556
Hydrogen . . . . .	5,500
Carbonic acid . . . . .	13,585

Graham believed, as a result of his experiments, that the passage of gases through rubber is not a simple process of diffusion, but that they are first liquefied in the pores of

<sup>1</sup> *Phil. Trans.*, 1866, p. 399.

the material, penetrate through the latter in the liquid state, and are then given off on the other side of the membrane. Later experiments by Ditmar<sup>1</sup> and others indicate, however, that ordinary diffusion takes place, complicated perhaps by adsorption phenomena. Naturally the permeability will vary considerably according to the nature of the mixing and porosity of the finished product. "Pure" rubber mixings (*i.e.* those compounded from rubber and sulphur only) are by no means the least porous. Denser mixings can be obtained by the addition of small quantities of such materials as paraffin, pitch, bitumen, etc.

The question of permeability to gases is an important one in connexion with the modern development of the dirigible balloon, and the literature on the subject is a rapidly growing one. Rosenhain and Barr,<sup>2</sup> in a report from the National Physical Laboratory, have described an apparatus for testing balloon fabrics for hydrogen permeability, and among the results obtained the following may be quoted:—

#### PERMEABILITY OF BALLOON FABRICS TO HYDROGEN

(*The tests were carried out at 15°*)

Description of Fabric.	Weight in grms. per sq. metre.	Permeability in litres per sq. metre per 24 hours.
Diagonal doubled cotton with three layers of rubber . . . . .	328	2.3
Parallel doubled cotton with two rubber layers . . . . .	226	13.5
Parallel doubled cotton with two rubber layers . . . . .	245	18.0
Diagonal doubled cotton with two rubber layers . . . . .	275	14.0
Diagonal doubled cotton with two rubber layers . . . . .	300	4.5
Diagonal doubled cotton with two rubber layers . . . . .	333	4.6
Parallel doubled cotton with two layers of rubber . . . . .	241	8.6
Goldbeater skin of different thicknesses.	301 to 91	0.1 to 0.4

<sup>1</sup> *Lectures*, pp. 207 *et seq.*

<sup>2</sup> *I.R.J.*, 1910, vol. xl. p. 288; cf. also *G.Z.*, 1911, vol. xxv. pp. 638 and 678.

*Effect of Light*

The effect of light, particularly of the more refrangible rays, is of great importance in connexion with balloon fabrics. V. Henri<sup>1</sup> has made an important contribution to our knowledge of this subject. He found that crude<sup>2</sup> rubber is much more susceptible to the action of the ultra-violet rays than vulcanized material, twenty hours' exposure sufficing to bring about visible deterioration of the former, whereas a much longer time (forty-eight to seventy-two hours) was required to produce any effect on the latter. "Pure" rubber was found to be more readily attacked than goods made with mineral fillers, and in the latter case deterioration was limited to the surface. Litharge restricts the change, antimony sulphide tends to promote it. Henri further found that in the absence of oxygen no deterioration takes place; the effect, therefore, is one of oxidation brought about or hastened by the ultra-violet rays. Henri comes to the general conclusion that crude rubber should not be used for balloon fabrics, that the cloth employed should be coloured with an ultra-violet screen such as chrome yellow, and that a rubber mixing containing a yellow pigment should be employed for the coating. These recommendations of Henri have already, I believe, been put into practice in modern balloon work.

### III. MECHANICAL PROPERTIES OF RUBBER

It is in its mechanical or tensile properties that the chief value of rubber as an industrial material lies. In its behaviour towards forces of extension or compression rubber occupies a unique position. A high grade soft rubber

<sup>1</sup> *Le Caoutchouc et la Gutta-Percha*, 1910, vol. vii. p. 4371; and *J.S.C.I.*, 1910, p. 1169.

<sup>2</sup> Crude rubber recovered from a solvent is much more susceptible to attack than rubber which has not been treated by a solvent. This is in accord with the general knowledge concerning the inferiority of rubbers that have been treated with, or recovered from, solvents.

extends to roughly ten times its original length before breaking; at the breaking point such a rubber will bear a load equivalent to about 10 tons to the square inch; if the tension is released shortly before the breaking point is reached, the material will, after a short period, contract to practically its original length. A piece of well-made rubber (*e.g.* a buffer) may be compressed many thousands of times to about one-third of its original thickness without any lasting effect. No other material is known which will behave, even within the widest limits, in this manner.

Needless to say, the mechanical properties of rubber vary widely according to the nature of the mixing. This variation is not, as I shall show later, merely one of degree. There are distinct and well-marked variations of type.

The general laws regarding the behaviour of high class soft rubber under stress were investigated by Stévert.<sup>1</sup> He employed a red, soft rubber made from fine Para and slightly "mineralized." The specific gravity of the material was from 1060 to 1065, and it is described by Stévert as being one of the best types of rubber used for industrial purposes. It is a pity that no further details concerning its composition are recorded, but it is obvious, from its behaviour, that it was a high grade soft rubber. The following<sup>2</sup> is a brief résumé of the general laws concerning extension and compression formulated on the basis of Stévert's work:—

#### A. Extension

(a) The effect of the load is inversely proportional to the cross-sectional area.

This law was first proved experimentally by Stévert, and was shown by him to hold good for strips or rings of a cross-sectional area up to 102 mm., and varying in regard to ratio of breadth to thickness from, roughly, 1:1 to 1:2.

<sup>1</sup> A. Stévert, *Résumé des Expériences sur l'Elasticité du Caoutchouc Vulcanisé*, *Bulletin du Musée de l'Industrie*, 1870.

<sup>2</sup> Cf. Schidrowitz, *I.R.J.*, March 22 to May 31, 1909, vol. xxxvii.

Stévert worked with intermediate loads—that is to say, he stopped short of the breaking strain, but the later joint-work of Dalén, Frank and Marckwald, and Schopper has shown that the law holds good for the full load of rupture for rings 4 mm. wide and varying in thickness from 2.5 to 7.5 mm. It would be of interest to determine experimentally the limits of the ratio  $b:t$  (breadth to thickness) for which the law holds good, but the general experience of the writer is that for a ring-shaped test-body a ratio of 10:1 is probably not excessive for rings not exceeding 10 to 15 mm. in breadth.<sup>1</sup>

The fundamental importance of the law enunciated above is obvious. If the stated relation between load and cross-sectional area did not exist, it would be practically impossible to compare any two samples not exactly similar in all dimensions.

(b) The total extensibility (*i.e.* elongation at break) is independent—certainly within the limits of the dimensions stated above—of the cross-sectional area.

Frank and Marckwald examined on the Schopper machine rings obtained from four different types of mixings, varying in cross-sectional area from 10 to 30 square mm. and in total elongation (at break) from 180 to 850 per cent., and found that the law held good in every case.

(c) Extensibility is not directly proportional to the load, but increases with equal increments of load up to a certain maximum point and then decreases. This maximum point is independent of the cross-sectional area.

According to Stévert, the maximum for the material examined by him was reached when a strip had been extended to double its original length. Moreover, the load necessary to produce an elongation of 4 (taking the original length as 1) was three times as great as the load producing an elongation of 2.

It is evident that  $P^2$  (the load necessary to double the

<sup>1</sup> The results obtained by Schwartz (*Journ. Inst. Elect. Engin.*, 1907 on "flexible" strip confirm this view.

original length) may be expressed in terms of cross-sectional area thus—

$$P^2 = ES,$$

where  $S$  is the cross-sectional area and  $E$  a constant dependent on the nature of the rubber. By determining  $P^2$  and  $S$  experimentally we can obtain  $E$  by calculation. This constant, for soft rubbers, is the mean value of the "modulus of elasticity."

(d) The relation between the extension of a band and the load producing the extension is a complicated one, the curve representing the relation being probably of a higher order than the third power.

This curve may be plotted in the usual way by determining corresponding values of  $x$  and  $y$  (load and length) experimentally. In the case of the material examined by Stéwart, the point of inflexion of the curve was found in every case (irrespective of cross-sectional area) to correspond to the co-ordinates

$$x = ES$$

$$y = 2 l_0^{-1}$$

More information is gained, however, by taking the abscissa ( $x$ ) in terms of load per unit of cross-sectional area, and in this way, of course, specimens differing in area may be compared. By taking the inclinations of the tangents at the various points to the curve so obtained, we get figures representing increments of length per unit of load, and from these figures we can readily obtain values for the modulus of elasticity.

(e) The load necessary to produce a specific extension is proportional to the cross-sectional area.

(f) The modulus of elasticity of rubber is a varying and not (as is the case with metals) a constant quantity.

Stéwart showed that in the case of his material that the modulus was greatest (*i.e.* it corresponded to a minimum of distensibility) when the load was at a minimum, and was

<sup>1</sup>  $l_0$  = original length of the test piece.

then equal to approximately 0.168 kilos. As the load increased the modulus decreased, and attained a minimum—one-third of its maximum value, namely, 0.056 kilos—at the moment when the length of the band under stress was double the original. It then increased up to the breaking point, passing twice through the mean value of 0.084 kilos.

(g) The maximum distensibility is accurately represented by the formula

$$e = x \frac{l_0}{ES},$$

in which  $x$  is a constant, which will vary with the quality of the rubber. This (*cf. supra*) is the elongation for 1 kilo added at the moment when the strip has attained double its original length.

From the above data it is possible to calculate the coefficient of "elastic resistance"  $\frac{R^2}{E}$  where  $R$  is the stress supported by the unit of area, and  $E$  is the modulus of elasticity.

By calculating this coefficient at an appropriate point, Stévert was able to demonstrate mathematically the superiority of rubber over steel where a yielding resistance (for instance in the case of railway buffers) is required.

### B. Compression

Practically speaking, rubber is an incompressible substance, and in this respect resembles other homogeneous colloids and water. According to Clapeyron, its compressibility is 0.00009295 of its original volume for a pressure of 1 kilo per sq. cm., that is, roughly, double the compressibility of water, but Thompson and Tait and Stévert were of opinion that it does not differ appreciably from water. Stévert showed experimentally that the volume of a mass of vulcanized rubber remains constant, whatever deformation of shape it may undergo. Thus, in the case of a buffer the mean diameter will increase in the same proportion as the area of the meridian section diminishes.

When rubber is compressed under conditions permitting lateral expansion, it behaves exactly like a fluid confined within a very resistant elastic membrane. Under ordinary conditions the original shape of the article compressed is maintained; that is to say—as Stévert has well put it—the sections at right angles to the compressing force increase but remain similar to one another. If we compress a disc, it retains its disc shape, *i.e.* it spreads equally in all directions; if we compress a square plate, it remains square in section; a rectangle remains a rectangle, and so on. Deformation may, however, take place under certain conditions. Thus, in the case of a buffer, if  $h$  is equal to or greater than  $\frac{3}{2}e$  ( $h$  standing for height and  $e$  for thickness), the inner surface becomes concave, that is, the buffer deforms. The same phenomenon occurs if two buffers whose joint height exceeds  $\frac{3}{2}e$  are placed over one another. In practice this is well known, and where a greater resistance than that obtainable from a single buffer is required, a number of buffers are employed, separated from one another by a rigid diaphragm.

The general equation illustrating the behaviour of a buffer to a compressive force is

$$h = \sqrt{\frac{H}{\frac{KHP}{S} + 1}}$$

When  $H$  = original height.

$h$  = Height under compression by force  $P$ .

$P$  = Force.

$S$  = Surface of buffer base ( $S = c^1 e$ , where  $c^1$  is the mean circumference and  $e$  the thickness) and  $K$  a constant dependent on the quality of the material employed.

Stévert's results generally have been amply confirmed

by later workers<sup>1</sup> and apply, broadly speaking, to all high class soft rubbers. Laws *a*, *b* and *e* (p. 221) apply practically to all types of rubbers, but no more than a brief consideration is necessary in order to appreciate the fact that laws *c*, *d*, *f*, and *g* cannot in an unmodified form apply to all types of mixings. Apart from the formulation and proof of the fundamental laws *a*, *b*, and *e*, the most interesting part of Stévert's researches dealing with *extension* is that demonstrating the nature of the soft rubber curve. The salient features of the curve (cf. Figs. 16–21) are as follow: At the beginning of the curve the extensibility increases with equal increments of load up to a point, termed by Stévert the *point of inflexion*. This point is reached when the rubber has been stretched to double its original length. After this the extensibility gradually decreases, and, as the breaking point is approached, it sinks to a minimum. The behaviour of soft rubber under stress is, therefore, entirely different from that of comparatively rigid materials, such as metal or wood. Broadly speaking, such materials offer the greatest resistance in the initial stages of the application of a progressive load, and, as the breaking point is approached, give way rapidly. The curve of a rigid material tends to run parallel with the abscissa (stress) with a slight inclination towards the ordinate (elongation), and, immediately before the break, turns sharply towards the latter. F (Fig. 17) is an illustration of this type of curve, and it will be observed that the difference in type between this curve and the soft rubber curves (*e.g.* Fig. 16; D, Fig. 17) is very marked indeed. F (Fig. 17) was a low grade hardish grey rubber.

Memmler<sup>2</sup> suggests that the characteristic form of curve described by Stévert can only hold good for pure fine Para mixings, but while it must be remembered that Stévert has said nothing which would involve the assumption that the

<sup>1</sup> Cf. Hinrichsen and Memmler, *op. cit.*; Breuil, *Le Caoutchouc et la Gutta-Percha*, 1904, vol. iii. p. 56; Schidrowitz, *loc. cit.*; Frank, *Lectures*, p. 289; etc.

<sup>2</sup> Hinrichsen and Memmler, *op. cit.*, p. 226.

characteristic curve is applicable to any and every kind of mixing, my own experience indicates that it broadly holds good for all high class soft rubbers, at any rate so far as the general form of the curve and the position of the point of inflexion are concerned.

I have referred above to the factor  $\frac{R^2}{E}$ , on which Stévert laid considerable stress, and which, according to him, represents "resistant elasticity" or stored energy. The calculation

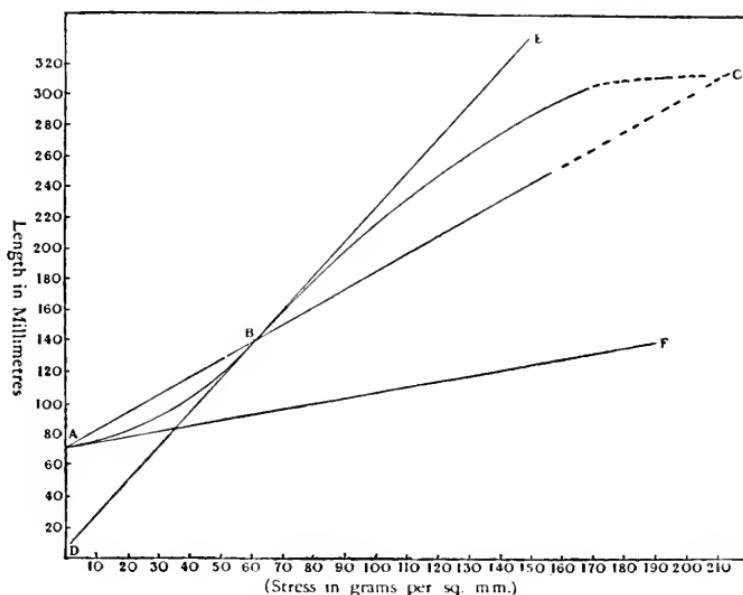


FIG. 16.—Typical (medium soft) Rubber Stress Curve  
(method of calculating values by tangents)

or rather interpretation of this factor, which should be a valuable asset in comparing different rubbers *inter se* or rubber with other materials, presents certain difficulties. The following explanation may therefore not be superfluous. In Fig. 16 the method of calculating  $\frac{R^2}{E}$  is indicated.<sup>1</sup> The

<sup>1</sup> R is the load (found by experiment) which will just extend the test piece to double its original length. It is therefore a fixed quantity. E, which is a variable quantity, is the load which, at any given point on the curve, will pro-

curve A B C represents the behaviour under stress of a fairly good class soft rubber examined in my laboratory. This rubber, it may be mentioned, is the sample described as A in table on p. 235.

It will be seen that the value of R, that is, the stress per unit area at the point where the rubber doubles its original length, is 0.06 kilos. In order to calculate the values of E (the modulus of elasticity) tangents are drawn to this curve at various points. The values of the tangents are as follow. At the commencement of the curve the value of the tangent

is a minimum and amounts to  $\frac{l_0}{\frac{22}{7}R}$ . As we proceed up

the curve we obtain at a point parallel to the straight line, A B C, a value of  $\frac{l_0}{R}$ . At the point of inflexion B, that is to say, where the curve reverses its direction, the value becomes  $\frac{19l_0}{10R}$ . From these figures the value of the modulus

E at different points may be calculated. The only value, however, which interests us is that at B, namely, the point of inflexion. This will be found as follows :  $E = \frac{10}{19}R = 0.032$ ,

from which we find  $\frac{R^2}{E}$  is equal to 0.113.

It should be borne in mind that for a rubber of this class, as Stévert found, E is a variable quantity, whereas the modulus of elasticity in the case of metals is up to a point shortly before rupture practically a constant. In the case of metals this modulus can only be ascertained by calculation, due an increase in length equal to  $l_0$ , that is the original length of the test piece. R is therefore equal to E at the point A (Fig. 16). According to our definition of E, a tangent drawn at any point on the curve equals  $\frac{l_0}{E}$ . It follows, therefore, that the value of E may be ascertained by the equation

$$E = \frac{l_0}{\text{Value of tangent}}.$$

The value of the tangent may, of course, be calculated by the ordinary graphic method.

and is of course then comparable to the value  $R$  in the case of a rubber such as is described above. That is to say, it is the value for the unit-area load which will double the length. In calculating the value of  $\frac{R^2}{E}$ , the object in regard to  $R$  is to obtain a value which shall denote either a limit of elasticity or a definite point of inflexion. In the case of soft rubbers which possess practically no limit of elasticity, Stévert adopts the latter method and takes the value of  $R$  as the load per unit area at the point of inflexion, and calculates  $E$  at the same point on the curve. This method of comparison of Stévert's is liable to give rise to some confusion, inasmuch as the value of  $R$  for metals is not the unit-area load capable of doubling the length of the material, whereas in the case of soft rubbers this is generally the case. The reason why Stévert took  $R$  at the unit-area doubling load was because at that particular point the rubber curve showed an inflexion. If the rubber worked on by Stévert had shown a point of inflexion elsewhere, then  $R$  would not have been equal to the unit-area doubling load, but would have been the value calculated at that point. If this had been so, the confusion between  $R$  and the modulus of elasticity  $E$  as applied to rigid materials could not have arisen, but if it is borne in mind that  $R$ , both in the case of rubber and of metals, by this method of calculation is either the limit of elasticity or the point at which the curve shows a change of sign, the matter becomes reasonably clear.

As I have already indicated, I am able to confirm from my own experience the fact that good soft rubbers show a point of inflexion on the stress curve almost exactly at the point where they double their length. This will be seen to be the case in regard to rubbers A (Fig. 16), D (Fig. 17), M49 (Fig. 20) and I (Fig. 21), and it will also be observed that it is approximately true in regard to the high class but rather harder samples B<sub>1</sub>, B<sub>2</sub> (Fig. 20). On the other hand, the rule does not hold good for the low

grade rubbers E and F (Fig. 17), and the same applies to the solid tyre rubber (Fig. 18).

If the rubbers which do not show a point of inflection are carefully regarded, it will be seen that they present an entirely different type of curve. For instance, rubbers E and F (Fig. 17) show curves which in their general nature are similar to the curves which one would expect from a more or less rigid material.

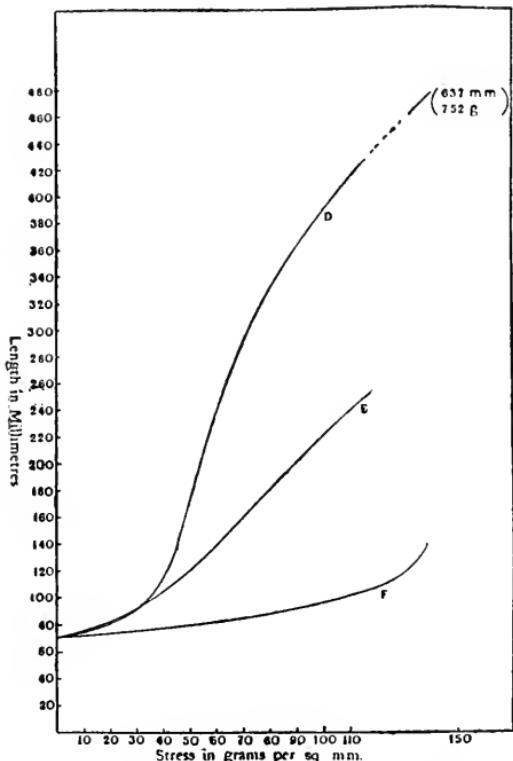


FIG. 17.—Tensile (stress) Curves up to Breaking Point

D=Cut sheet (soft) band

E=Low grade red sheet

F=,, hardish grey sheet

Note distinctly different types of curves

They proceed in practically a straight line and then turn upwards, whereas in the case of the soft rubbers or of the rubbers which I may perhaps refer to as not "denatured," the curve does not show any approximation to a straight line at the beginning but turns sharply upwards, then reverses its sign, continues steeply for a time, and then gradually turns away inwards from the ordinate. This, of course,

means that the modulus of elasticity at the commencement is relatively high, that it then becomes smaller but fairly constant for a considerable period, and that it subsequently increases in value up to the break. These figures bear out what might be anticipated from theoretical con-

siderations, namely, that by varying mixings we may entirely change the nature of a rubber, that is, change it not only in degree but also in kind. The rubbers which have not been "denatured" show a relatively high degree of yield when stress is first applied, and then strenuously resist further extension up to the break. The rubbers which have been "denatured" show a considerable and approximately constant resistance at first, and then very rapidly give way for equal increments of load.

The facts referred to above are not merely of theoretical interest, they indicate that by experimental means we are able to obtain a deep insight into the nature of a rubber

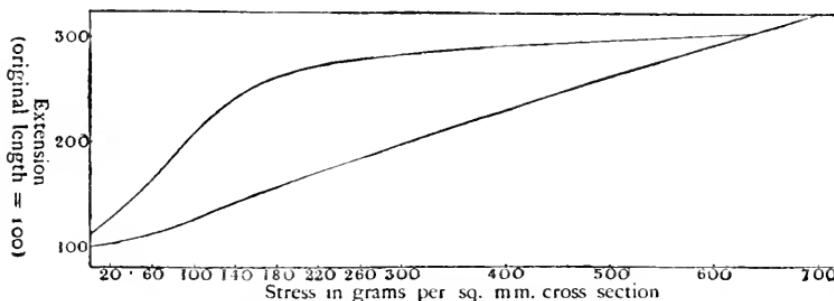


FIG. 18.—Hysteresis Loop, solid tyre rubber. Note the "hard" (flat) nature of curve, as compared with soft rubber

and they further show how the general laws regarding a soft rubber must be modified for other varieties.<sup>1</sup> The results which I have obtained so far appear to indicate that there are three distinct types of curve, namely—(1) A normal "soft" or high class rubber curve (such as that in Fig. 16); (2) a rigid type of curve such as F (Fig. 17); and (3) an anomalous type of curve such as E (Fig. 17). These

<sup>1</sup> Breuil (*Le Caoutchouc et la Gutta-Percha*, 1904, pp. 77-80) arrived at somewhat similar conclusions on the basis of the examination of four rubbers. He also investigated the tensile properties of a number of unvulcanized and vulcanized mixings, and the results indicated that for mixings containing 50 per cent. or more rubber, vulcanization increases both tensile strength and extensibility. With less than 50 per cent. of rubber, the tensile strength increased, but the extensibility decreased. In view of the conditions under which Breuil tests were made they must not be taken as formulating any general law.

types of curves may be well illustrated by reference to the factor  $\frac{R^2}{E}$ . With regard to the curve of type (1), I have already shown above how the values of R and E are found. In brief, R, for all practical purposes, is taken as the area-unit load which will double the length of the rubber, and E is the value obtained by calculation from the tangent to

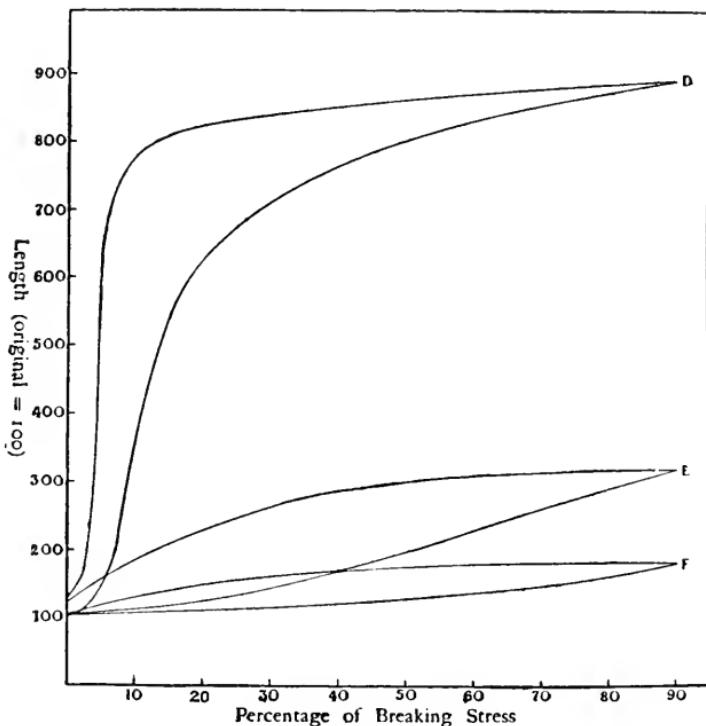


FIG. 19.—Hysteresis Loops of a high class soft (D) rubber, and of two low grade rubbers (for particulars, see p. 235). Note different shapes of loops

the curve at the point of inflexion. With regard to curves of type (2) I suggest that R should be regarded as the limit of elasticity, that is to say, it should be taken at the point at which the curve commences to deviate seriously from a straight line. This value may either be found from the curve or obtained from the experimental figures. In either case the method is fairly simple: R represents the point

at which the unit increment of load commences to produce appreciably enhanced elongation. Similarly, in curves of type (2),  $E$  may either be calculated—taking it as the unit-area load which will produce a doubling of length—or may

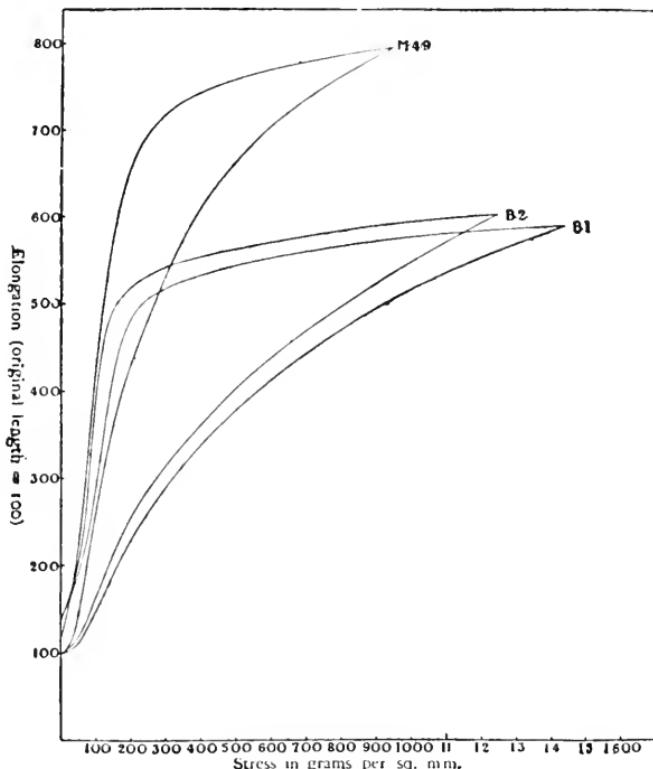


FIG. 20.—Hysteresis Loops at 70 per cent. of Breaking Load

M49 is a soft, highly distensible rubber of fair strength, containing rubber and sulphur only

B1 and B2 are hardish rubbers of great strength, but of moderate distensibility, containing 35 to 40 per cent. of mineral matter

B2 (which is otherwise the same mixing as B1) contains about 5 per cent. of "oil substitute" (see p. 240)

be got directly from the curve by producing the straight part sufficiently. With regard to curves of type (3) (such as E) neither of these methods appears able to give a satisfactory result, for the curves possess neither the character

of the normal "soft" curve (1) or of the rigid type (2). The problem may, I suggest, be solved by regarding R as the limit of elasticity, and by determining this experimentally by some conventional method. For instance, I have calculated R in the case of rubber E by assuming that the limit of elasticity is connoted by the "coefficient of resiliency" figure, which is obtained by determining the minimum unit-area load which will under certain standard conditions produce a sub-permanent set. E is then calculated in the usual manner as in the case of the rigid type (2).

R and E together with some other values were obtained by working with a series of rubbers, of which the following is a brief description:—

- A. 85 parts fine Para, 15 parts of a sapotaceous gum; 10 parts sulphur; a soft high class mixing; *ash nil.*
- B. Grey cut-sheet band; high class soft rubber; *ash nil.*
- C. Particularly fine crude plantation Para; *ash nil.*
- D. Grey rubber band (cut sheet) similar to B; *ash nil.*
- E. Low class red sheet. *Ash* 41.5 per cent.
- F. Low class rather hard grey sheet. *Ash* 57.5 per cent.
- G. Good specimen of grey solid tyre. *Ash* 30 per cent.
- H and J. Medium class fairly strong grey sheet. *Ash* 49.2 per cent.
- K. Somewhat similar to H and J. *Ash* 56.0 per cent.

(Where the statement "ash nil" appears above, this is not to be taken literally, but to indicate that the ash is a mere trace—that is, not exceeding 1 per cent., an amount referable to the slight impurities in the raw materials from which these mixings were made.)

The results obtained were as follow:—



The values of R and E were calculated for rubbers A, B, C, and D according to method 1; for H, J, and K according to method 2. In the case of E method 3 was adopted. In the case of F, methods 2 and 3 were applied and the same result was obtained in both cases. Curve G was at first believed to belong to type I, but from the general behaviour of the rubber, and from the other ex-

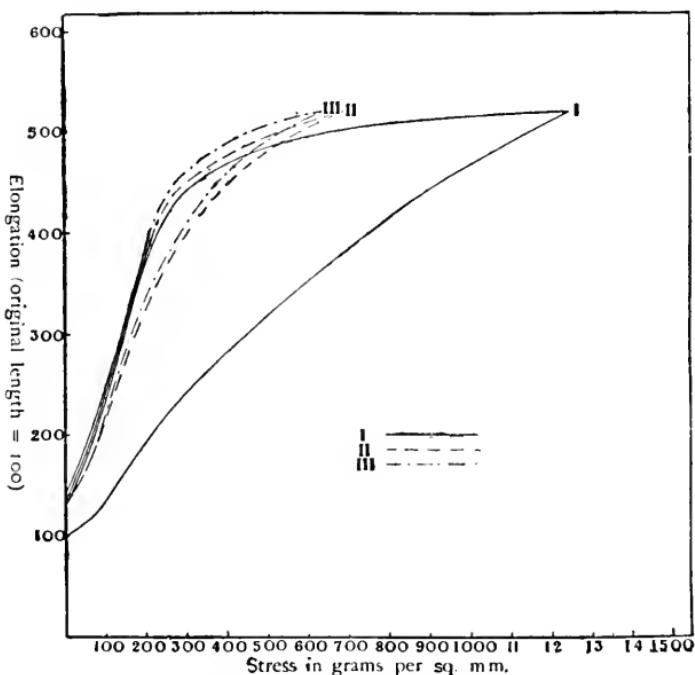


FIG. 21.—Three Cycle Hysteresis Loops at 70 per cent. of Breaking Load on high tensile rubber (see p. 245). Cycles II. and III. are practically identical

periments made with it, I came to the conclusion that the figures derived from method 1 were in this case not applicable. It was obvious that method 2 was also not in point. Method 3 was therefore applied, and this gave results which appeared very fairly to indicate the nature of this rubber.

With regard to the values other than E and R recorded on page 235, the figures under column 4 represent the

decrease in tensile capacity at the end of one hour after loading the rubbers to 70 per cent. of the breakings stress. This test was suggested to me in conversation by Dr. Frank,<sup>1</sup> and I believe that if adopted it would turn out to be of great utility. I have applied this test in the following manner. A ring-shaped standard test body is loaded on the Schopper machine<sup>2</sup> to, say, 70 per cent. of its breaking stress—the latter being determined by a previous experiment. The ring then remains stretched at the length corresponding to this stress for an hour, the lever of the machine meanwhile continuing to act. From time to time the diminution of the load is noted. The results so obtained indicate the degree to which the rubber becomes "denatured," or the diminution of its capacity to support a load at a fixed length and over periods of time. The results are numerically very striking. Rubber D, at the end of an hour, showed a decrease of only 15 per cent., rubber F a decrease of 30 per cent., and rubber E a decrease of 40 per cent. When we consider that the breaking stress of D is roughly six times as great as that of E and F, these results become still more striking. Values  $\frac{C}{D}$  and  $\frac{F}{D}$  were suggested as capable of giving useful results by Schwartz.<sup>3</sup> C represents the elongation produced by a definite unit-area load D, and F represents the residual elongation after the load has been removed. These values may therefore be obtained in conjunction with the hysteresis<sup>4</sup> test. The results given above were obtained by stressing the rubbers up to 90 per cent. of their breaking load, and subsequently gradually removing the load as already explained. The value  $\frac{C}{D}$  represents elongation per unit-area load, that is to say, the elongation which is produced by, say, a pound or a kilo or a gramme for every unit of cross-sectional area at a load representing

<sup>1</sup>Cf. Schwartz, *Journ. Inst. Elect. Engin.*, 1910, pp. 717 *et seq.*

<sup>2</sup>Cf. Chap. XVI. p. 278.

<sup>3</sup>*Journ. Inst. Elect. Engin.*, 1907.

<sup>4</sup>See below, p. 243.

90 per cent. of the total breaking load. Schwartz suggests that  $\frac{C}{D}$  and  $\frac{F}{D}$  will give figures roughly representing the amounts of rubber in different mixings made with the same rubber, but I think that this can only be the case within extremely narrow limits, inasmuch as C and D are dependent upon so many conditions apart from the quality of the rubber. On the whole, I think that  $\frac{C}{D}$  is a value which is not likely to be of much practical importance, excepting perhaps for comparative purposes within a limited range of material, but that the value  $\frac{F}{D}$  is a useful one, as it indicates permanent or sub-permanent set per unit of load. It will be noticed that in the case of the high class rubber D, the figure is a very small one; in the case of rubber E, which is soft and yet obviously of low quality, the figure is very high. Again, in the case of G, which is a good class solid tyre of fair strength, the figure is also relatively low.

#### INFLUENCE OF THE NATURE OF THE MIXING ON TENSILE PROPERTIES

A number of investigations<sup>1</sup> on the influence of mineral and organic fillers on the mechanical properties of rubber have been published, but the majority of the results obtained are open to serious criticism, owing either to the fact that the conditions of vulcanization of the test pieces were of an unsatisfactory character, or that the methods of testing employed were not of a nature to inspire confidence. It is all the more to be regretted, therefore, that in one of the very few investigations conducted on scientific lines—I refer to the work of Memmler and Schob<sup>2</sup>—the composition of

<sup>1</sup> Pahl and Heinzerling, *loc. cit.*, p. 216; Breuil, *Le Caoutchouc et la Gutta-Percha*, 1904, pp. 77, 80; Ditmar, *G.Z.*, 1905-6, vol. xx. pp. 394, 579, 678, 760, and vol. xxi. p. 103; Schwartz, *Journ. Inst. Elect. Engin.*, 1910, p. 726-8.

<sup>2</sup> *Mittheilungen aus dem Kgl. Materialprüfungsamt*, 1909, vol. iv.

the samples employed is not given. The object of the authors of the work in question was, however, mainly to determine the influence of the nature of the test piece in tensile work, and with this end in view they selected six typical commercial rubbers. Put briefly, they desired to investigate the general laws applying to typical rubbers and not the effect of specific ingredients in the mixings. The same object was in my mind when I undertook the work, of which a brief description is recorded on pp. 234-238.

With regard to the influence of the nature of the rubber in a mixing, and also of the presence of a small quantity of "oil substitute," the following data and results—hitherto unpublished—may be of interest. The samples, kindly prepared for me by Mr. P. L. Rothband of the Unity Rubber Company, were typical high tensile rubbers. The compositions of the mixings were as follows:—

	Type 1.	Type 2.
Rubber . . . .	100	100
Zinc oxide . . . .	70	70
Oil substitute . . . .	0	10

In addition, of course, each mixing contained suitable vulcanizing materials. The cure, in each case, was the optimum time at 40 lb. pressure. Allowing for the vulcanizing materials, type 2 contained approximately 5 per cent. of "substitute."

Specimens were tested in the form of rings on the Schopper machine, with the results given on the following page.

It will be noticed that the effect of the small quantity of "substitute" in the mixings is very marked throughout. The decrease in tensile strength of the samples made with "substitute" is not proportional to the amount present,

but is considerably greater, and on the average approximates to 15 per cent. The extensibility (elongation) is slightly increased by the substitute. The hysteresis curves in Fig. 20 show the results obtained by stressing B1 and B2

Nature of Rubber in Mixing, etc.	Breaking Strain (lb. per sq. inch).	Elongation at Break (original length = 1).
A. Fine Hard Para . . .	3108	6.88
AI. Do. with "substitute"	2647	7.10
B1. Plantation Sheet . .	2928	6.83
B2. Do. with "substitute"	2563	7.18
C. Cameta Negro Heads . .	2720	6.38
CI. Do. with "substitute"	2339	6.46
D. Red Kassai . . .	2708	7.08
DI. Do. with "substitute"	2354	7.34

to 70 per cent. of the breaking load. For the sake of comparison, a very soft rubber, M49, is included in the figure. It will be noticed that the effect of the "substitute" generally is to soften and weaken the rubber, the result being a more upright curve, and a hysteresis loop of relatively greater area. Fig. 21 shows repeated hystereses of rubber CI.

#### TENSION AT CONSTANT ELONGATION

Schwartz<sup>1</sup> made a series of interesting tests on the influence of the rubber content on tension at constant elongation, at atmospheric and high temperatures respectively. Working at 180° F. over periods of six to forty-eight hours, at a constant elongation of 100 per cent., he found that, for under-cured specimens containing 88 per cent. Para, the deterioration was less than in specimens containing 66 per cent., whereas for normally cured or over-cured specimens the position was reversed. With a series of materials prepared by another maker, containing 30, 40, and

<sup>1</sup> *Op. cit.*, pp. 717 *et seq.*

50 per cent. of rubber respectively, he found that over a range of temperature from 150° F. to 200° F., and under the same conditions of tension as in the first series, the deterioration (expressed as percentage decrease in tension from the third to the sixth hour) for normally cured specimens was less in the case of the high grade rubbers than in the lower grade one. At 200° F. the deterioration was practically the same for all specimens. In the experiments at atmospheric temperatures, the results were found to differ appreciably from those at high temperatures. At the end of the test period—four weeks—the results, as might have been expected, were decidedly favourable all round to the better grade (88 per cent. Para) rubber. The 66 per cent. specimens correctly vulcanized deteriorated less rapidly than the under-cured samples, but more rapidly than those that were over-cured. Schwartz considers these experiments somewhat inconclusive, but if I may venture a criticism, it is to the effect that with relatively high grade rubbers, such as those examined, results of a more characteristic nature would have been obtained by working at greater elongations. At an elongation of 100 per cent. the capabilities of a high grade soft rubber are not at all severely tried (cf. Tables on pp. 235 and 240).

### EXTENSION AT CONSTANT LOADS

Schwartz<sup>1</sup> applied the investigations of Bouasse<sup>2</sup> and Phillips<sup>3</sup> on the slow extension of rubber under a constant load to a number of specimens containing from 30 per cent. to 60 per cent. of Para. Using the formula

$$x = \alpha + b \log t$$

in which  $x$ =extension at a given time  $t$ ,  $\alpha$  the initial extension in the first time unit (1 minute), and  $b$  the increment of extension with time due to the slow extension, he found

<sup>1</sup> *Op. cit.*, pp. 722 et seq.

<sup>2</sup> *Annales de la Faculté des Sciences de Toulouse*, vol. ii.

<sup>3</sup> *Phil. Mag.*, 1905, vol. ix. p. 515.

the numerical values of  $\alpha$  and  $b$  for the different rubbers to be:—

Mixing.	$\alpha$ .	$b$ .
60 per cent. Para . . .	30.5	2.5
50 , , . . .	13.8	1.0
40 , , . . .	8.9	0.6
30 , , . . .	4.0	0.3

### INFLUENCE OF DEGREE AND METHOD OF VULCANIZATION

The comparative experiments of Schwartz on the effect of the degree of vulcanization have been referred to above. These experiments, of course, dealt only with a small part of this important question, and it is to be hoped that more work in this direction will be forthcoming. Weber<sup>1</sup> obtained curves from four rubbers possessing the following coefficients of vulcanization:<sup>2</sup> 1.78; 2.14; 2.87; and 4.4 respectively. Specimen one was obviously much under-, specimen four much over-cured. Within the limits of his experiments he found that as the coefficient of vulcanization increases, the strength of the material is improved, but that the elasticity is diminished. If a rubber exhibits a high vulcanization co-efficient and low strength, combined with high elasticity, it is probable that the mixing has been over-worked. If the elasticity is faulty, then, Weber concluded, it is probable that the mixing contains a considerable quantity of "reclaimed." On the whole, Weber considered that under-cured goods are more liable to deterioration than over-vulcanized materials, particularly if much mineral matter or "oil substitute" is present.

<sup>1</sup> *The Chemistry of India-Rubber*, pp. 283 *et seq.*

<sup>2</sup> The coefficient of vulcanization is a figure obtained by expressing the combined sulphur as a percentage of the pure rubber in a mixing.

I have had occasion to study the effect of variation of time, temperature, and style of vulcanization on a number of mixings, and also the effect of modifying the composition of the latter within certain limits, and as a result of the experimental work carried out so far, I can vouch for the fact that it is an extremely difficult and complicated business to obtain results from vulcanization experiments on a sufficiently broad basis for the formulation of general laws. I refrain, for the present, therefore, from publishing the results already obtained, for I feel that unless sufficient evidence is to hand to prove any one point up to the hilt, there would be little object in adopting this course. I may, perhaps, be pardoned for pointing out that there is a vast field of interesting and instructive research work to be done in this connexion.

### HYSTERSIS IN RUBBER

If a strip of rubber is extended by means of a load, and the extension is stopped before the breaking point is reached, it will be found, on removing the load, that the retraction curve (obtained in the ordinary way by plotting elongation against stress) does not coincide with the extension curve. The two curves form a "loop" (cf. Figs. 18-21), the area and base of which will vary according to the degree and time of tension, the nature of the mixing, etc. This phenomenon has been termed *hysteresis* on account of its similarity to the well-known effect obtained when magnetised iron is de-magnetised. The retraction curve does not end at the point at which the tension curve started, and the distance between these two points may, in a sense, be regarded as a measure of the hysteresis effect. In other words, after the removal of the load the strip of rubber is longer than it was originally. This increase in length is termed the "set." This "set" gradually decreases if the strip is allowed to rest, and is called the "permanent set" if no further contraction takes place after an adequate time

interval, and "sub-permanent set" if it is measured at some specified time short of the "permanent set." According to Stévert, there is no such thing as a "permanent set" in the case of a perfectly vulcanized soft rubber, and if this statement is not absolutely accurate, it approximates very closely to the truth, provided that the material has not been stressed beyond a certain maximal point. I may point out at once that as a measure of quality, the "permanent" or "sub-permanent" set is, except within the very narrowest limits, a very misleading factor, particularly if employed to compare different rubbers which have been stressed to a fixed percentage of the respective breaking loads. For instance, a high class soft rubber breaking at, say, 2000 lb. to the square inch, if stressed to 90 per cent. of the breaking load, will almost with certainty show a greater "set" than a low grade rubber breaking at, for instance, 700 lb. The explanation is that in stressing a high grade rubber to a definite percentage of its breaking stress, the absolute load applied, and therefore the absolute work done in the rubber are far greater than in the case of the low grade material. This is made quite clear by Fig. 19. Rubber D, the breaking strain of which is nearly six times as great as that of F, shows a decided set, whereas in the case of F the set is very small indeed, in fact barely visible on the scale to which the illustration is drawn. It will be noticed, however, that in order to stress D to 90 per cent. of the breaking load, the rubber must be extended to more than *eight times* its original length, whereas the length of F is not even doubled. The point is an important one, inasmuch as specifications for contracts have been drawn without taking recognition of this fact.

#### NATURE OF HYSTERESIS LOOPS

As characteristics of the attributes of a rubber, the general configuration (type) and area of the loops, and the relationships of area to load and elongation, are of far

greater importance and interest than the "set." The factor  $\frac{\text{set}}{\text{work done}}$  may, however, be useful for purposes of comparison in many cases. Fig. 19 shows loops<sup>1</sup> of the rubbers referred to above, and it will be noticed that the configuration or type of loop D is entirely different from loops E and F. Loop D is concavo-convex, loops E and F are of a double convex type. The difference between the two types of curves would have been accentuated if they had been drawn to unit-area load, but this was not done, for the simple reason that loop D would have been so large as to become, for purposes of reproduction, almost unmanageable. In Fig. 20 three hysteresis loops are shown. M49 is a very soft (extensible) rubber of fair strength; B<sub>1</sub> and B<sub>2</sub> (cf. p. 240) are high tensile, hardish rubbers. The loops are quite characteristic. The soft medium class rubber gives an upright loop of relatively small area; the strong but hardish rubbers give larger and flatter loops. In each case the rubber was stressed to 70 per cent. of the breaking load. Fig. 21 illustrates a hysteresis experiment comprising three successive cycles. In this case also the rubber was stressed to 70 per cent. of the breaking load. It will be observed that constancy is approached after cycle 2.

#### EFFECT OF TEMPERATURE ON HYSTERESIS

Shedd and Ingersoll,<sup>2</sup> in the course of some interesting work on hysteresis, or, as they termed them, *viscosity*, loops, examined the effect of temperatures varying from 11° to 93° on the nature and area of the loop. With increasing temperature the area of the loop became smaller over the whole range. Up to a temperature of 60° the extension curves gradually became flatter with increasing temperature, but beyond this point their general disposition does not vary appreciably. That is to say, while the work done

<sup>1</sup> For other characteristics of these rubbers, cf. Table, p. 235.

<sup>2</sup> *Physical Review*, 1904, vol. xix. (2), p. 107.

during extension is not appreciably affected by raising the temperature from  $60^{\circ}$  to  $90^{\circ}$ , the work done during retraction gradually increases.<sup>1</sup>

### COMPARISON OF LOOPS

Schwartz,<sup>2</sup> who has made several important contributions to our knowledge of hysteresis in rubber, suggests the following procedure for reducing the salient features of various hysteresis loops to a common basis for purposes of comparison:—

1. The designation of the form of extension as convex, linear, concave, or convex-concave.
2. The determination by means of a planimeter or area scale of the area representing the work done in extending the rubber.
3. The determination of the work done by the rubber in retracting.
4. The reduction of the areas in 2 and 3 to their equivalent triangles on a given base.

For the methods of calculation suggested by Schwartz, the reader is referred to his original communication.

### SUCCESSIVE CYCLES

According to Schwartz, the dominant character of the second cycle, and all subsequent cycles, is that the first is concave to the axis of load in all cases. For purposes of comparison, it is preferable to take the successive cycles to the same maximum load and not to the same maximum extension. The results obtained by Schwartz (working at a constant load equivalent to a primary extension of 150 per cent.) indicate that the higher the quality of the rubber, the more quickly approximate constancy between successive cycles is attained.

<sup>1</sup> For the effect of high temperatures, cf. Bouasse, *op. cit.*, and Schwartz, *op. cit.*, p. 735.

<sup>2</sup> *Op. cit.*, p. 705.

## CHAPTER XV

### CHEMICAL ANALYSIS AND PHYSICAL EXAMINATION OF RUBBER<sup>1</sup>

#### A. ANALYSIS OF CRUDE RUBBER

THE commercial analysis of crude rubber is useful from two distinct points of view. In the first place, it is of assistance to the crude rubber producer for the purpose of controlling and improving the quality of his output; and, secondly, it is useful to the manufacturer as a guide to the price which he can afford to pay for the material, and to its applicability in the manufacture of various grades of goods. Occasionally problems arise, for the solution of which the methods of ordinary commercial analysis are inadequate, and in such cases the investigator must be guided by his own experience and the available literature.

Before commencing an analysis of a crude rubber, the analyst should be quite clear concerning the aim of his work. As a rule, a complete or detailed analysis is, in commercial work, unnecessary. It is also useless, if the analysis is to be of assistance in the buying and selling of a specific parcel of rubber which has to be disposed of

<sup>1</sup> It is not my intention to make any attempt in this chapter to give a complete or detailed account of the analytical and physical methods which have been devised with a view to the examination of crude or vulcanized rubber, and of the other materials employed in rubber mixings. My object is to give those who are interested in this subject a general idea of the methods available, and their bearing on practical questions, and to enable them, as far as I am able, to discriminate between that which is good and that which is bad.

within two or three days, to apply methods involving a week or a fortnight's work, however superior they may be from a scientific or technical point of view. This appears obvious enough, on the face of it; but processes which can have no other than a commercial application—if any—have from time to time been proposed, and much belauded, which are perfectly hopeless from a practical standpoint.

It is, I think, undeniable that a certain amount of experience and general knowledge regarding rubber are essential in the vast majority of cases, if the analysis is to have any practical value. I refer rather to the interpretation of results than to the analytical operations as such, although even such comparatively simple determinations as those of resin and moisture are not free from specific difficulties.

#### *Analysis on "Washed" or "Unwashed" Sample?*

The question as to whether the analysis of a crude rubber should be carried out on the material as such, or after "washing," has been the subject of some debate, the chief arguments in favour of working on "washed" material being that the latter represents the rubber as ready for use in the factory, and that a more reliable sample can be drawn than is the case where the uncleared material is employed. My experience, however, tends to show that no hard and fast rule can be laid down; much plantation rubber is not washed in the factory, and it is therefore unreasonable and a mere waste of time to apply the washing process to rubber of this class prior to analysis. Frequently, also, samples submitted are so small as to make washing an impracticable and, indeed, a misleading operation, for the loss during "washing" of even a minute quantity of rubber, will, in the case of small samples, vitiate the whole of the analytical results. In dealing, however, with dirty, wet, tacky, or obviously heterogeneous material, it is practically essential that the analysis should be carried out on a washed sample. It is difficult to wash rubber samples satisfactorily, except

on a power-driven experimental washing machine,<sup>1</sup> but the fact is that almost every branch of rubber work involves the use of special apparatus and machinery, and those who desire to devote themselves to rubber work must make up their minds to a considerable initial capital outlay.

### QUALITATIVE TESTS

Occasionally problems arise which involve the application of qualitative or semi-qualitative tests. For instance, it may be necessary to ascertain the origin or nature of a sample. Quantitative estimations of resin, proteid, etc., may be of some utility in this connexion, particularly if the analytical figures are read in the light of the physical characteristics and of the appearance, odour, etc., of the material, but the results obtainable in this way are of a general rather than of a specific character. For practical purposes, the only tests of a more or less specific character available are those bearing on the nature of the resins, and the state of aggregation of the material. The resins, after extraction, may be examined in regard to optical activity,<sup>2</sup> solubility, saponification, iodine absorption, homogeneity (by "re-crystallising"), and melting point. It is important, also, to note whether the resin is generally of a hard or soft character. It is true that the data in the literature of this question available as a guide are scanty, but, as a rule, it is only a question of determining to which of two or possibly three varieties a rubber belongs, and parallel experiments with resins extracted from the varieties in question should, in such cases, yield the necessary supplementary information. By collating the results of the ordinary quantitative determinations, of the resin tests, of the viscosity determinations, of the observations regarding general physical characteristics, and such knowledge of the history of the sample as are available, a fairly reliable

<sup>1</sup> I employ for this purpose a pair of 9 inch by  $4\frac{1}{2}$  inch rolls driven by a 5-H.P. motor.

<sup>2</sup> Cf. reference, p. 141.

conclusion may, in the great majority of cases, be reached.

### QUANTITATIVE DETERMINATIONS

In commercial analysis it is generally sufficient to make determinations of MOISTURE, RESIN (acetone extract), MINERAL MATTER, NITROGEN, INSOLUBLE MATTER, and RUBBER. These determinations should, in my opinion, always be supplemented by an estimation of VISCOSITY. Occasionally it may be desirable to make a quantitative analysis of the main ash constituents or a determination of combined oxygen. I need scarcely add that in many cases a determination of no more than one or two of the constituents referred to is ample.

#### *Moisture*

The most satisfactory method of determining moisture is by means of a vacuum desiccator *in the cold*, either on strips of washed crêpe or on the original sample cut into small pieces. This method, unfortunately, is very slow, and for this reason is generally inapplicable in ordinary commercial analysis. If a vacuum drier is available, the sample may be dried at a temperature which should not exceed  $35^{\circ}$  to  $40^{\circ}$ , but the vacuum should be applied gradually, for otherwise a skin or dry rubber is liable to form on the surface, which impedes the further process of drying. If no more than a very rough estimation of moisture is desired, the sample may be heated in the water oven at a temperature of about  $80^{\circ}$  until it ceases to lose weight. The figure so obtained does not actually represent the amount of moisture present, as oxidation takes place from the beginning of the heating. As a rule, the most convenient method of estimating moisture is by difference, namely, by weighing the residue left from the acetone extraction. The weight of the original specimen being known, and the weight of resin and residuum ascertained, the loss obviously represents moisture.

*Determination of Resin*

Resin is best determined in a direct extraction apparatus provided with a mercury seal, such as that shown in Fig. 22.<sup>1</sup> The flask may be heated by a direct flame through a piece of thin asbestos board. It is easier to regulate the boiling this way than on the water bath, and although I have made very many hundreds of estimations, not a single accident has taken place. As a rule, the process of extraction on a sample of 3 grms. is complete after five to six hours' boiling, but I employ a standard time of eight hours.<sup>2</sup> After the extraction has been completed, the solvent is distilled off, and the residue weighed in the usual manner.

*Determinations of Nitrogen and Ash*

These constituents are determined by the ordinary analytical methods, nitrogen on 1 to 2 grms. of the sample, ash on 3 to 4 grms. The determination of ash should partake as far as possible of the character of a dry distillation, that is to say, the products of decomposition should not be allowed to ignite. This is best accomplished by placing the dish in which the material to be ashed is contained on an asbestos millboard containing a small central hole, through which the preliminary heating is carried out.

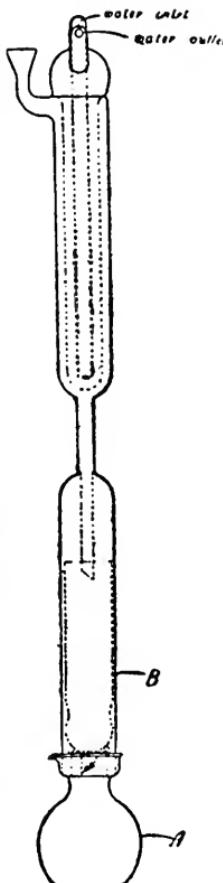


FIG. 22.—Extraction Apparatus

<sup>1</sup> Cf. Schidrowitz and Kaye, *J.S.C.I.*, 1907, p. 127.

<sup>2</sup> Cf. *G.Z.*, 1911, vol. xxv. p. 716.

*Determination of Insoluble Matter*

It has been suggested by Ditmar<sup>1</sup> and others that insoluble matter should be estimated directly by weighing the residual material filtered off from a more or less dilute benzene solution of the rubber,<sup>2</sup> but, in my opinion, it may be estimated more conveniently indirectly. This operation is best carried out on the residuum from the acetone extraction, but in the case of sticky rubbers it is more convenient to work on the original sample. The method I apply is as follows:—About  $\frac{1}{2}$  to 1 grm. of fresh or extracted material is accurately weighed, and is then treated in a narrow 200 c.c. measuring cylinder with 200 c.c. of benzene. The cylinder is shaken at intervals, but the analyst must use his judgment as to when "solution" is complete. Two to three days are generally ample for this purpose. The liquid is allowed to settle over night, and in the majority of cases a considerable volume of absolutely clear fluid above the finely divided insoluble matter is then available. An aliquot proportion (20 to 50 c.c.) of clear liquid is pipetted off, evaporated on the water bath, and the residue then dried and weighed. The difference between the weight of the dried residue and the equivalent weight of the original sample obviously represents insoluble matter. The great advantage of this process over processes in which insoluble matter is directly weighed, lies in the fact that it is extremely difficult to wash out all the rubber from the insoluble matter, and that a small quantity of rubber remaining on the filter or in the filtering tube may obviously lead to very grave errors.

*Determination of Rubber*

Rubber may be determined by difference by subtracting the figures obtained for moisture, resin, and insoluble matter from the total. The results so obtained are no more than

<sup>1</sup> G.Z., 1905, vol. xx. p. 364.

<sup>2</sup> Cf. Spence, *Q.J. Reprints*, No. 10, 1907; and *Analyst*, 1907, p. 424.

an approximation. To begin with, neither the mineral matter or the nitrogen are, according to my experience, entirely or invariably insoluble. It seems that a certain proportion of mineral matter may pass into colloidal solution, and the same applies to a part of the nitrogen. The same objections apply, of course, to the estimation of rubber on the basis of the figures obtained by evaporating off an aliquot part of the clear solution referred to under *insoluble matter*. I think, however, that the latter is the preferable method. Various methods have been suggested with a view to estimating the rubber direct, as nitrosate or tetra-bromide, and such methods may have a certain value in special cases, for instance where it is doubtful whether the material which is soluble in benzene (after resin extraction) is rubber at all. These methods have been much discussed in recent publications,<sup>1</sup> but as I think that they possess, at present at any rate, no material practical advantage over the methods already discussed, I am content to refer the reader to the publications indicated should he desire to make use of them for any special purpose.

Schneider<sup>2</sup> attempted an evaluation of quality by dissolving in chloroform and precipitating fractionally with alcohol. In this way he obtained so-called  $\alpha$ ,  $\beta$  and  $\gamma$  modifications, of which, according to him, the  $\alpha$  is the most valuable part of the rubber, the  $\gamma$  modification the least valuable. I quite fail to perceive any theoretical or practical basis to this method, and as far as I am aware there is nothing to indicate that the rubber substance is not essentially a homogeneous material.

### *Physical Determinations*

The general method of ascertaining the viscosity of crude rubber has already been described.<sup>3</sup>

Direct tensile tests on crude rubber are not, in my

<sup>1</sup> Cf. Hinrichsen and Memmler, *op. cit.*, pp. 95 *et seq.*; and O. Korneck, *G.Z.*, 1910, vol. xxv. pp. 4, 42, and 47; also *J.S.C.I.*, 1910, vol. xiii. p. 21; and *Analyst*, 1911, p. 27.

<sup>2</sup> *G.Z.*, 1903, vol. xvii. p. 74

<sup>3</sup> Cf. p. 158, and *J.S.C.I.*, 1909, p. 3.

opinion, to be recommended, although at one time I was inclined to believe that something of the kind was within the realm of practical work. Even the most perfect sheet is not sufficiently homogeneous for tensile work, and in the case of crêpe or other forms of rubber, it is, of course, quite out of the question.

### COMMERCIAL VALUATION

A commercial valuation cannot be undertaken on the basis of chemical analysis alone, but if the figures obtained by analysis are read in conjunction with the data obtainable from a physical examination, it is generally possible to form a very fair idea of the value of the material. Whenever practicable, the chemical and physical tests should be amplified by vulcanization experiments, for, after all, its behaviour on vulcanization is the ultimate test of value of a rubber from the point of view of the manufacturer. It is impossible within the scope of this volume to say more with regard to vulcanization tests than this: there is no standard short method applicable in all cases. To obtain the best results, particularly on a rubber from a new source of supply, the vulcanization experiments must extend over a range of methods (open cure, press cure, etc.), of time, temperature, and of different mixings. Nevertheless, it is generally possible, with some experience, to gather valuable preliminary information regarding vulcanizing capacity by employing a mixing of rubber with 10 per cent. of sulphur, and applying an open cure at 45 lb., samples being withdrawn at certain intervals of time.

### B. ANALYSIS OF VULCANIZED RUBBER

#### *Sampling*

The preparation of a sample of rubber for analysis is by no means a simple matter. Hardish rubbers can, as a rule,

readily be reduced to fine flakes or powder by breaking up on the experimental mixing rolls, or, if these are not available, by passing (after cutting into small pieces) the material through an ordinary domestic mincing machine, and subsequently through a coffee grinder. The sample may also be obtained by rasping, but this is an exceedingly tedious operation. These methods are, however, not to be recommended for soft rubbers, as they all involve considerable heating of the material, which, in its turn, may lead to a decided increase in the resin (acetone extract) figures and otherwise affect the composition of the sample. Soft rubbers are, therefore, best cut up into very small pieces, with the scissors or in some other suitable manner.

#### *GENERAL SCHEME OF ANALYSIS*

The general scheme of analysis suggested by Weber,<sup>1</sup> which was founded mainly on the researches of Henriquez,<sup>2</sup> and amplified by his own work, may still be regarded as the most convenient and useful guide in commercial rubber analysis. Weber's scheme is given on p. 256.

It is not, as a rule, necessary to carry out the whole of the operations described in this scheme. Light-coloured goods cannot well contain any of the constituents under C (Tar, etc.), and if there is any doubt on this point, a preliminary test may be made by warming a part of the sample with chloroform or benzene. If tar, bitumen, or similar substances are present, the solvent will become brown and (generally) fluorescent. Frequently the extraction with nitro-naphthalene (or one of the more suitable solvents referred to below<sup>3</sup>) can be omitted, and in this event the mineral matter is estimated on the original sample

<sup>1</sup> *Chemistry of India-Rubber*, 1902 (Griffin).

<sup>2</sup> *Chem. Zeit.*, 1892, 1893, and 1894, and *Z. f. angew. Chem.*, 1899, p. 802.

<sup>3</sup> Starch and dextrose are rarely present, but if suspected, preliminary qualitative tests should be applied. Free carbon (lamp-black) can only be present in dark-coloured goods. If fibrous materials are suspected, a part of the original sample may be dissolved in petroleum or xylene and the residue examined.

I. Extraction with Acetone (on a 2·3 grm. sample).		VI. Separate Estimations.					
A. EXTRACT.	B. RESIDUE.	C. EXTRACT.	D. RESIDUE.	E. EXTRACT.	F. RESIDUE.	G. EXTRACT.	H. RESIDUE.
Resins. Mineral oils. Resin oils. Solid hydro-carbons (paraffin, etc.). Free sulphur.	II. Extraction with Pyridine. <sup>1</sup>	Tar. Pitch. Bitumen. Sulphur in above.	III. Extraction with Alcoholic Potash.	" Oil substitutes." " Blown " oils. Sulphur in substitutes. Chlorine in substitutes.	IV. Extraction with Nitro-Naphthalene. <sup>1</sup>	V. Extraction with Boiling Water.	I. EXTRACT. Starch. Dextrine.
						Rubber, gutta, and balata. Combined sulphur. (The above are estimated by difference.)	K. RESIDUE. Mineral matter. Free carbon. Fibres. Mineral sulphur.

<sup>1</sup> See remarks below.

by ignition. The following abbreviated scheme of analysis may, in many cases, be employed :—

Extraction with Acetone.			
A. EXTRACT.	B. RESIDUE.	Extraction with Alcoholic Potash.	
Resins. Free sulphur. Oils, etc.	C. EXTRACT.	D. RESIDUE.	Rubber. Combined sulphur. Mineral matter.
Separate Estimations.			
MINERAL MATTER, by ignition or by dissolving residue D in a suitable solvent and weighing residue ; or by dissolving a part of original sample and		weighing residue. RUBBER, by difference, or as bromide (from residue D or original sample). COMBINED SULPHUR (in residue D).	

### *Extraction with Acetone*

The extraction (on 2 to 3 grms. of the sample) is carried out in the same apparatus as that employed for estimating resin in crude rubber (cf. p. 251). A clean, light-coloured extract, from which the free sulphur crystallizes sharply, indicates the absence of "substitutes" and other organic fillers. The examination of the acetone extract for solid hydrocarbons, mineral oils, etc., the estimation of these constituents and of "free" sulphur fall within the realm of general analytical chemistry.<sup>1</sup>

### *Extraction with Pyridine*

Both Esch<sup>2</sup> and Ditmar<sup>3</sup> have shown that pyridine may dissolve very considerable quantities of rubber, and quite recently Britland and Potts<sup>4</sup> have published a paper from

<sup>1</sup> Cf. Weber, *loc. cit.*; Hinrichsen, *op. cit.*, pp. 108 et seq.; E. W. Lewis, Allen's *Commercial Organic Analysis*, 1911, vol. iv. 4th ed. (London, Churchill).

<sup>2</sup> *G.Z.*, 1906, vol. xx, p. 324.

<sup>3</sup> *Ibid.*, p. 441.

<sup>4</sup> *J.S.C.I.*, 1910, p. 1142.

which the conclusion must be drawn that pyridine is usually quite inadmissible for the extraction of bitumen and similar substances. Pontio<sup>1</sup> suggests the use of a mixture of 40 per cent. spike oil (dextro-rotatory lavender oil) and 60 per cent. acetone, the extraction taking place *after* the treatment with alcoholic soda. I have no personal experience of the method.

#### *Treatment with Alcoholic Potash*

This is carried out by boiling the rubber (after removal from the extraction shell in which it has been submitted to the action of acetone) in a flask for three to four hours with 50 c.c.  $\frac{N}{2}$  alcoholic potash. After washing and drying, the loss in weight, according to Weber, very accurately represents the weight of the fatty substitutes removed by saponification. This statement, however, requires qualification. Considerable quantities of mineral matter, such as zinc oxide and antimony sulphide may be rendered soluble by the treatment, and, moreover, most commercial substitutes contain a certain proportion of acetone soluble substances. It is in every case desirable to examine the alcoholic potash extract for the presence of fatty potash salts (soaps), by acidifying the liquid after driving off the bulk of the alcohol and making up with water, extracting with ether and separating the fatty acids from the ether extract in the usual manner. This method may be made approximately quantitative. An approximate idea of the quantity of "substitute" may be obtained by determining the ash in the rubber before and after extraction, and allowing for the loss so indicated in conjunction with the total loss of weight of the material. When antimony sulphide or vermillion are present, this method is inapplicable, and in such cases I have found the most convenient method to be that of determining the metals in the alcoholic solutions by any convenient method. Weber states that the

<sup>1</sup> *Bulletin Soc. Chim.*, 1909, pp. 428 *et seq.*, and *Analyst*, 1909, p. 329.

rubber residue, after extraction, should be dried in a current of coal gas, to avoid oxidation, but in the majority of commercial analyses this is an unnecessary refinement. If the residue, after washing with hot water, is finally washed with alcohol and then with ether, it dries very rapidly. Moreover, certain constituents of coal gas are readily absorbed by rubber, and if, therefore, very accurate results are required, the drying should take place in a current of hydrogen.<sup>1</sup>

#### *Residue from Alcoholic Potash Extraction*

Weber, for certain reasons, recommended—with a view to the separation of rubber, sulphur of vulcanization, and combined chlorine from mineral matter, fibres, starch, etc. (see Table, p. 256)—that the residue from the alcoholic potash treatment should be heated in melted  $\alpha$  nitro-naphthalene at a temperature of  $180^{\circ}$ . According to Weber, rubbers containing even as high a vulcanization coefficient as 15 per cent. are readily dissolved in this manner, the rubber being, however, destroyed (not merely dissolved) by the process. After solution is complete the melt is diluted with benzene and filtered. The method is, however, highly inconvenient; it is difficult to avoid charring, the solutions frequently filter very badly, and there are other drawbacks which need not be discussed. With a view to avoiding the disadvantages of the nitro-naphthalene treatment, Frank and Marckwald<sup>2</sup> worked out a method which consists substantially in heating the material at a pressure of 12 to 15 atmospheres with xylene in an autoclave, and subsequently diluting with ether and filtering. Hinrichsen and Manasse<sup>3</sup> recommended the use of petroleum<sup>4</sup> (B.P.  $230^{\circ}$ - $260^{\circ}$ ) at atmospheric

<sup>1</sup> For the determination of the other substances that may be present in the alcoholic extract, see Weber, Hinrichsen and Lewis, *loc. cit.*, p. 257.

<sup>2</sup> *G.Z.*, 1908, vol. xxii, p. 1344.

<sup>3</sup> *Chem. Zeit.*, 1909, vol. xxxiii, p. 735.

<sup>4</sup> The use of petroleum was suggested by Henriquez as long ago as 1892 (*Chem. Zeit.*, vol. xvi, p. 1624), and by Axelrod (*G.Z.*, 1907, vol. xxi, p. 1229).

pressure. The substance is heated at 180°–200° until solution is complete, and, after cooling, the liquid is diluted with light petroleum, and then whirled in a centrifuge. Frank and Marckwald<sup>1</sup> have suggested certain improvements on this method. A disadvantage of the use of petroleum, xylene, etc., at high temperatures lies in the fact that certain mineral constituents, such as antimony sulphide and magnesium carbonate, are decomposed. Hinrichsen<sup>2</sup> proposes to overcome this difficulty by employing solvents such as anisol or phenetol, which, according to him, readily dissolve rubber at 90°–120°. Pontio<sup>3</sup> employs cumene vapours for the same purpose. With regard to the above methods generally, my experience is that the use of a solvent, such as petroleum, possesses marked advantages over the  $\alpha$  nitro-naphthalene method suggested by Weber. The work is quicker and cleaner, the solutions obtained, as a rule, filter readily, and as the rubber substance is not destroyed, it is always possible (after filtering or settling), by working on an aliquot part of the clear liquors, to separate, either in the form of a bromide (Axelrod method) or as such, an aliquot proportion of vulcanized rubber.<sup>4</sup>

#### ESTIMATIONS OF SEPARATE CONSTITUENTS

I propose to deal briefly with the more important improvements on or modifications of the general methods described by Weber.

##### *Mineral Matter*

If the ignition method—which, for obvious reasons, is in many cases faulty—is used, the sample<sup>5</sup> should be very slowly heated in a crucible set in a hole cut in an asbestos plate, so that the products of distillation may not catch fire.

<sup>1</sup> *G.Z.*, 1909, vol. xxiii. p. 1522.

<sup>2</sup> Hinrichsen and Memmler, *op. cit.*, p. 126.

<sup>3</sup> *Loc. cit.*, p. 258.

<sup>4</sup> See p. 262.

<sup>5</sup> Frank and Marckwald; cf. Ditmar, *op. cit.*, p. 181.

When the material is thoroughly charred, it is strongly heated in the usual way until a carbon free ash is obtained. Methods of separating mineral matter as such have already been described above, and one or another of these should certainly be employed when substances such as antimony sulphide, vermillion, carbonates or sulphides are present. In some cases it is not necessary to go through the somewhat tedious operations involved in an actual separation of rubber from mineral matter (that is, as a part of the general scheme of analysis), but it is merely desired to determine certain specific mineral constituents, for instance mercury or antimony. It is obvious that in the instances mentioned this cannot be done by incineration. Frank and Jacobsohn<sup>1</sup> devised a process consisting essentially in the destruction of organic matter by means of nitric acid and potassium chlorate, the nitric acid being subsequently removed by evaporation with hydrochloric acid, and the antimony and mercury estimated in the filtrate. Subsequently Frank and Birkner<sup>2</sup> proposed to use as the oxidizing mixture nitric acid and a persulphate. Rothe<sup>3</sup> prefers to use Millons's well-known oxidizing mixture consisting of sulphuric and nitric acids.

#### *Total Sulphur*

For the estimation of total sulphur in soft and medium-hard rubbers, the exceedingly rapid and convenient sodium peroxide method<sup>4</sup> gives excellent results. If the Henriquez-Weber<sup>5</sup> fusion method is employed, deflagration and spitting may be avoided by heating the mass *prior to melting* for about an hour to 130° in an air oven.

<sup>1</sup> *G.Z.*, 1909, vol. xxiii. p. 1046; and Lewis, *op. cit.*, p. 142.

<sup>2</sup> *Chem. Zeit.*, 1910, vol. xxxiv. p. 49.

<sup>3</sup> *Mittheil. d. Kgl. Materialprüfungsamt*, vol. xxv. p. 105; *Chem. Zeit.*, 1909, vol. xxxiii. p. 679; and Hinrichsen, *op. cit.*, p. 127.

<sup>4</sup> Von Konck, *Z. f. angew. Chem.*, 1903 (16), p. 516; and *G.Z.*, vol. xviii. p. 730.

<sup>5</sup> The material is treated with strong nitric acid, the liquid evaporated to a syrup, sodium carbonate and sodium acetate added, and the residue (after evaporation and drying) melted, a few crystals of KNO<sub>3</sub> being added to completely burn off the residual carbon. Cf. Weber, *op. cit.*

## DIRECT ESTIMATION OF RUBBER

A reasonably correct estimation of rubber as such is of importance in the analysis of goods specified by contract to contain a definite proportion of the material, and in certain other contingencies. It is certainly a weak point in rubber analysis that up to the present no entirely reliable method of direct estimation, applicable in all cases, has been evolved. The indirect method may obviously give results very wide of the mark, as it may involve the sum of all the errors accruing from the determinations of the individual constituents or groups of constituents. This fact should be kept in view by the critics of some of the recently proposed direct methods of estimation. They appear ready to strain at the gnats of the direct, but quite satisfied to swallow the camels of the indirect methods. To Axelrod<sup>1</sup> must be given the credit of having evolved the first direct process, which, although by no means perfect and open to criticism on a number of points, gives at any rate within a limited sphere, according to my experience, very useful results, particularly if modified in certain details.

The salient points of Axelrod's method are as follow:— 1 grm. of the sample is dissolved in 100 cc. petroleum of high boiling point ( $230^{\circ}$ – $300^{\circ}$ ) by heating for a suitable period (one to three hours suffice, as a rule). The cooled liquid is shaken up and 10 c.c. are withdrawn with a pipette. To the 10 c.c. removed (=0.1 grm. original sample) 50 c.c. of Budde's bromine solution<sup>2</sup> are added, the liquid allowed to stand several hours, and then 100 to 150 c.c. 96 per cent. alcohol are added. After settling, the precipitate is washed, dried at a temperature not exceeding  $60^{\circ}$ , and weighed. The crude bromide so obtained contains an aliquot part of the mineral matter present in the sample, and this is determined by incineration of the bromide. The amount of ash found is subtracted from the weight of the crude bromide,

<sup>1</sup> *G.Z.*, 1907, vol. xxi. p. 1229; and *J.S.C.I.*, 1907, p. 1058.

<sup>2</sup> Sixteen grms. bromine + 1 grm. iodine in 1 litre of  $\text{CCl}_4$ .

and the difference X 314 (the factor suggested by Axelrod) represents the amount of rubber ( $C_{10}H_{16}$ ) present in the original sample. The bromide, it may be added, contains the whole of the sulphur of vulcanization.<sup>1</sup> Axelrod's method has been somewhat severely—in my opinion unduly so—criticized. The weakest point of the process is that if the sample contains mineral constituents liable to decomposition, modification or volatilization, the results may deviate very seriously from the truth. This difficulty<sup>2</sup> I have found may in the majority of cases be overcome in a very simple manner. If, instead of shaking up the petroleum solution after cooling, it is allowed to stand for about twelve hours, the supernatant liquor is, as a rule, almost bright. The bromide obtained from 10 c.c. of the cleared liquor contains so little mineral matter that the error introduced by its incineration is very slight. If the liquid resolutely refuses to clear, the desired result may generally be achieved by diluting the whole or an aliquot part with light petroleum. Rubbers containing antimony or mercury (red rubbers) cannot always be treated in the manner described, as the golden sulphide or vermillion contained tend to go into colloidal solution. In such cases—although I have no experience in this connexion—the use of a solvent of low boiling point might lead to the desired end. Harries and Rimpel<sup>3</sup> found by experiment that the whole of the rubber present in the petroleum solution is not converted into insoluble bromide, but the figures published by Axelrod show that this is certainly not always the case. My own experience with soft to medium hard grey rubbers is that the results, generally, are rather low, but that a very close approximation to the truth can be arrived at for this class of material by the equation

$$x = y + \frac{y}{10}$$

<sup>1</sup> By determining the sulphur (in the absence of sulphur in the mineral matter) the coefficient of vulcanization may be obtained.

<sup>2</sup> I refer to white, grey and black, but not to red rubbers.

<sup>3</sup> G.Z., 1909, vol. xxiii. p. 1370.

where  $x$  = actual percentage of rubber, and  $y$  = percentage of rubber found by the bromide method.

Hübener,<sup>1</sup> assuming (cf. p. 171) that rubber mixings contain varying quantities of "free" mono-sulphide and di-sulphide rubber, points out that di-sulphide rubber cannot combine with bromine at all, and that for this reason the Axelrod method may lead to grave errors, inasmuch as the di-sulphide molecules will not be precipitated by the bromination process. Whether this is so or not, it must be remembered that Hübener's theory regarding the composition of vulcanized rubber yet awaits confirmation. Nevertheless, the specific objections to Axelrod's method—(1) that the use of a constant factor for mixings varying enormously in regard to their state of vulcanization must produce more or less appreciable errors; (2) that a part of the rubber may escape precipitation—are by no means negligible. Hübener,<sup>2</sup> on the basis of his vulcanization theory, has evolved a somewhat complicated process depending on the estimation of bromine combining values and sulphur of vulcanization. According to him the presence of "substitutes," gutta-percha and balata are without influence, but from a recent paper<sup>3</sup> it would appear that when asphalt, bitumen, etc., or similar materials are present, the method requires modification. Hübener's results require confirmation before the method can be generally accepted. Alexander<sup>4</sup> proposes to determine the rubber in the form of the nitrosate. This, as is the case with the bromide, contains the whole of the sulphur of vulcanization. Substantially the same criticisms apply to the nitrosate as to the bromide methods.

Inasmuch as vulcanized rubber may be obtained in solutions in an apparently unaltered state, it seems somewhat remarkable that, until quite recently, no attempt

<sup>1</sup> *Chem. Zeit.*, 1909, vol. xxxiii. pp. 648 and 662.

<sup>2</sup> *Loc. cit.*, and *Chem. Zeit.*, 1910, vol. xxxiv. pp. 1307 and 1315; and *Analyst*, 1909, p. 365 and 1911, p. 75.

<sup>3</sup> *Chem. Zeit.*, 1911, vol. xxxv. p. 113.

<sup>4</sup> *Z. f. angew. Chem.* (18), p. 164, (20) p. 1355; and *G.Z.*, vol. xxi. p. 727.

appears to have been made to avoid the difficulties inherent in the bromide and nitrosate methods, by separating the vulcanized rubber from a convenient solution, purifying and weighing *as such*. The general lines of a method of this kind have now been indicated by Seidl<sup>1</sup> in the course of a highly suggestive paper dealing mainly with the action of litharge as a catalyst in vulcanization. Seidl dissolves the rubber in xylene under pressure, removes suspended mineral matter<sup>2</sup> (after settling has deposited the bulk of it) by shaking the xylene solution with hot 20 per cent. HCl, hot H<sub>2</sub>O, hot 10 per cent. KOH and again hot H<sub>2</sub>O successively, unites the wash liquors, extracts then with light petroleum, and adds the extract to the xylene solution. The mixed xylene and light petroleum solution is then steam distilled, the separated rubber taken up with ether, precipitated by means of alcohol, purified by kneading with alcohol, and weighed. It seems to me that on these general lines a very pretty process for determining vulcanized rubber as such should be evolved.

### PHYSICO-CHEMICAL TESTS

It is frequently in practice necessary to investigate the behaviour of rubber goods towards chemical reagents such as acids, alkalis, oils, etc. The general lines on which investigations of this nature are best carried out are as follow:—

- (1) Effect of the reagent on the weight and volume of the sample.<sup>3</sup>
- (2) Effect of the reagent on the tensile properties of the sample.

Changes in weight and volume may be conveniently determined on discs such as are obtained, for instance, in the course of punching test rings for tensile determinations. The weight and specific gravity of the disc are determined

<sup>1</sup> G.Z., 1911, vol. xxv. p. 712.

<sup>2</sup> The specific object in this case was to remove lead.

<sup>3</sup> Cf. Pahl and Heinzerling, *loc. cit.*, p. 216.

before and after exposure to the reagent, and from these data changes in weight and volume are calculated. The effect of the reagent on the tensile properties of the rubber is best determined by making parallel tests with rings before and after exposure.

## PHYSICAL TESTS

### *Heat Tests*

The old "Admiralty" test consists in subjecting the samples to a dry heat of  $132^{\circ}$  ( $270^{\circ}$  F.) for one hour, and to a moist heat (*i.e.* in steam) of  $160^{\circ}$  ( $320^{\circ}$  F.) for three hours. These and similar tests are conveniently carried out on test rings, as in the physico-chemical tests.<sup>1</sup>

### *Porosity*

Weber<sup>2</sup> proposed to express the porosity of a rubber by the formula

$$\rho = \left( \frac{\text{real specific gravity}}{\text{apparent specific gravity}} - 1 \right) 1000.$$

The "apparent" specific gravity is obtained by ascertaining the density of the material in the usual manner, the "real" specific gravity by reducing the rubber to a fine condition, weighing a definite quantity into the pyknometer, partly filling with water, evacuating with the pump to remove occluded air, filling up to the mark with boiled water and weighing at a standard temperature. An alternative method, which, I think, gives more reliable results, is to expose test pieces of known weight to the action of water at a pressure of several atmospheres for a

<sup>1</sup> Heat tests should not be applied indiscriminately to all classes of goods ; the object for which the rubber is intended to be used should be kept in mind. For instance, a door mat or tyre cover is not expected to resist high temperature steam. Nevertheless, the rational application of heat tests affords a useful measure of quality even in the case of articles which, in use, will not be exposed to other than atmospheric temperatures.

<sup>2</sup> *Op. cit.*, p. 226.

number of days. The pieces are then superficially dried with filter paper and weighed.

#### *Electrical Tests*

Rubber mixings (soft rubber or ebonite) that are intended for insulating work are subjected to certain electrical tests, particularly for insulation resistance (specific resistivity and surface resistance) and for dielectric strength (breakdown voltage). Materials which, when new, respond perfectly to the electrical tests, may, after being in use for a short period, break down badly owing to deterioration. It is most desirable, therefore, that electrical tests should be made in conjunction with or supplemented by chemical and chemico-physical tests such as are likely to throw light on the composition and liability to deterioration of the goods.

## CHAPTER XVI

### MECHANICAL TESTS

**I**N any reasonable collective consideration of the tests which are or may be applicable to india-rubber articles, mechanical tests must, for a variety of fairly obvious reasons, occupy an important position. The value of india-rubber articles is primarily due to the remarkable physical properties of the basis material. Tests which are directed towards ascertaining the mechanical condition of rubber goods, are a measure of, or deal with, *effect*. Chemical tests, as a rule, deal with *cause*. It is obvious that the first step is to ascertain whether an article is satisfactory or not; if the mechanical tests indicate unsatisfactory quality, then chemical tests must be used to ascertain why this is the case. It is true that the foregoing statement does not cover the whole ground, for the reason that, apart from its general mechanical (tensile) properties, india-rubber is also much used on account of its inertia towards air, water, and chemical substances. Where it is used in this connexion, chemical tests, or a combination of chemical, physical and mechanical tests, are obviously of primary importance. It is also, of course, the fact, that chemical tests are frequently desirable for the purpose of detecting a potential weakness, or for the examination of problems in regard to which no reliable physical or mechanical tests are at our disposal. Nevertheless, in the great majority of cases, mechanical tests are absolutely essential in the examination of materials made with or from rubber.

Mechanical tests comprise—(a) *General tensile tests*; (b)

*compression tests; (c) abrasion tests; (d) special tests for hardness and resiliency, etc.*

### A. TENSILE TESTS

The difficulties connected with the application of tensile tests to more or less rigid materials such as wood, yarns, metals, are well known; in the case of rubber these difficulties are enhanced by the peculiar properties of the material. This applies more particularly to the determination of breaking strain and elongation at break, but to a minor extent to observations on the behaviour of the material towards (relatively small) intermediate loads. The main problems to be considered are—(1) The nature of the test piece; (2) the method of gripping; (3) the method of applying the load, *i.e.* the nature of the tensile machine.

#### *The Test Piece*

Three methods of preparing test pieces are available, namely, moulding, cutting, or punching. Of these methods punching, provided the punches are sharp, gives the best results. For the preparation of ring-shaped test pieces the correct method is undoubtedly that of multiple-punching, as devised by Schopper. Moulded test pieces give lower figures than punched specimens, possibly on account of the difficulty of getting a perfect outer surface. The cutting of test pieces by hand is an exceedingly unsatisfactory operation.

For experimental work in the factory, a test sheet of a standard thickness (made up from carefully calendered material) should be vulcanized under conditions approximating as closely as possible to those to be applied to the bulk goods. If the object is to examine the properties of a particular rubber, the most suitable method is to vulcanize in an autoclave press, or, in the absence of this, in a plunger mould in steam, or in the ordinary hydraulic press.

The question arises as to how test pieces, which are to be examined by the buyer or consumer on a contract governed

by specification, should be prepared. It is frequently very difficult to obtain appropriate test pieces from the actual article. It has been suggested that in such cases—and, indeed, it is by no means certain that this would not be preferable in all cases—part of the mixing should be taken and vulcanized in sheet form in the press, under conditions approximating as closely as possible to those employed for bulk ; or, alternatively, vulcanized in the press on some conventional or agreed lines. The reply to this has been that there would be no guarantee to the purchaser that the test pieces so prepared would correspond to the bulk of the goods. I have myself in the past thought this was a serious objection, but a visit to America in 1909 convinced me that this is only another example of a theory which breaks down entirely in practice. They have found over there—and, indeed, at least one of the Government departments has adopted this method—that it is quite feasible to have a special test piece pressed or moulded in this way. The test piece is accepted as corresponding to bulk if the general results of *chemical analysis* of the test sheet correspond to the results obtained with the bulk of the goods. If simple chemical determinations, such as those of the amount of mineral matter, resin, and of saponifiable matter, etc., are found to correspond, it is practically out of the question that the bulk should have been made from a mixing different from that employed for the test piece. If a specially prepared test sheet is not available, appropriate sections (for instance, from a solid tyre, buffer or valve) must be cut in the lathe or by some other available method.

The shape of the actual test piece is of primary importance. Only two general forms need, however, to be considered, namely, the prismatic rod with enlarged ends—such as is employed in the testing of metals—and the ring. The main disadvantages of the rod form are—(1) Crushing in the jaw or “grips” is bound to take place if the material is gripped sufficiently to prevent slipping, and the break occurs in or close to the jaw ; (2) if insufficiently gripped the

material slips, and the automatic measurement of elongation becomes impossible. These difficulties may, in a measure, be overcome if it is only desired to ascertain the breaking strain and to obtain an *approximate* idea of the elongation at break, but even within these limits the rod-shaped test piece is very unsatisfactory. Good breaking strain results may be obtained with a test piece of the shape indicated in Fig. 23a, but it is not practicable to obtain elongation measurements in this manner. With a rod-shaped test body of the style shown in Fig. 23b, elongation measurements of a kind may, with certain types of rubber, be obtained by following up with the callipers two lines, drawn on and well within the prismatic part of the test piece, but reliable breaking strain results cannot be got. With the ring-shaped test body, on the other hand, provided the ring is almost a perfect section of a hollow cylinder, and that it rotates<sup>1</sup> while it is being extended, entirely reliable results for breaking strain, elongation at break and intermediate values, can be obtained.

The ring-shaped test-body appears to have been first used by Stévert,<sup>2</sup> who worked with a stationary ring suspended between smooth hooks. A great improvement over this method was effected by Schopper,<sup>3</sup> who, at the suggestion of Prof. Dalén, devised means (see below) whereby the ring is evenly rotated during the application of tension.

#### *Method of Punching Rings*

Plate XXXVIII, A shows the type of punching machine constructed by Schopper for cutting rings in two operations.

<sup>1</sup> See p. 275.

<sup>2</sup> *Loc. cit.*, p. 276.

<sup>3</sup> Cf. Frank, *Lectures*, p. 209; and Hinrichsen and Memmler, *op. cit.*, p. 171.

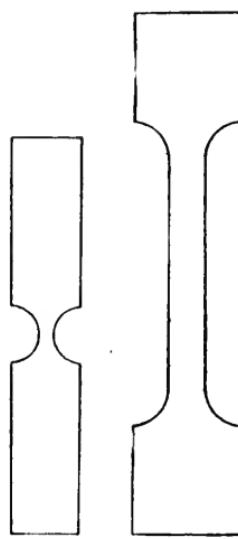


FIG. 23a      FIG. 23b  
Test Pieces, rod form

A disc is punched from the test sheet with the larger cutter (Fig. 24 A), the material resting on a movable boxwood base. The disc, which has a diameter of 52.6 mm., is then centred

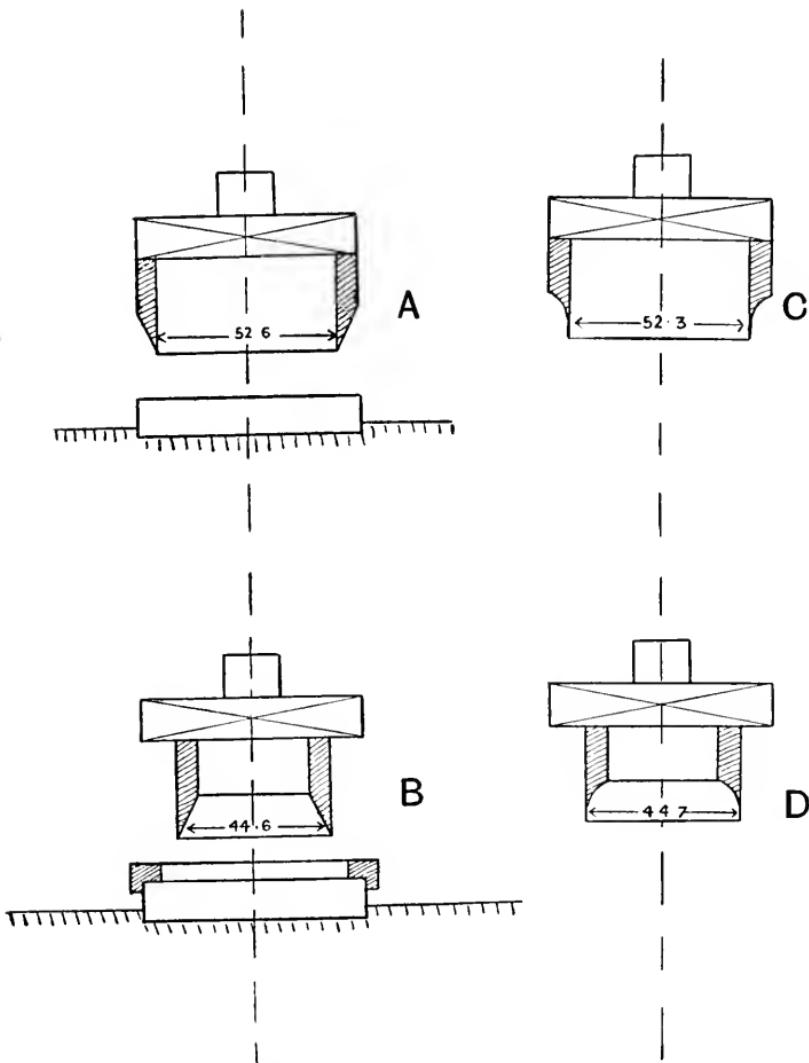


FIG. 24.—Schopper Cutters for punching Test Rings. A and B old, C and D new, style

in a cylindrical metal ring, which is previously fitted on to the boxwood base (Fig. 24 B). The smaller cutter (diameter, 44.6 mm.) having been fitted to the punch, a smaller disc is cut

from the larger one, a ring 4 mm. broad being thus obtained. In practice this method of obtaining rings has proved satisfactory for medium to hardish rubbers, but with soft rubbers a ring with a decidedly concave outer surface—that is to say, not possessing a true rectangular section—is formed. Memmler and Schob<sup>1</sup> have overcome this difficulty by cutting the ring in three instead of two operations, and by substituting for the rectangular (section) centring ring a ring sloping inwards, so as to give the necessary play to the material at the moment of punching. The cutters employed are of a more slender type than in the older form, and have diameters respectively of 56.3, 52.3, and 44.3 mm. (Figs. 24 C and D). A further improvement is that the boxwood base is abolished, the rubber resting on a thin (1 mm.) disc of cardboard laid on the polished base of the press. In this manner rings of absolutely rectangular section and 4 mm. wide may be obtained from any type of rubber.

Memmler and Schob<sup>2</sup> carried out an admirable and exhaustive piece of work on the influence of the form of the test piece in tensile work; the following is a brief summary of the results obtained by them:—

1. *Rod-shaped Bodies.*—(a) For soft high class rubbers it is practically impossible to use the rod form at all, inasmuch as the break almost always takes place in the jaw or in the “head” piece.

(b) The shape of the rod does not appear to influence the breaking strain figures appreciably, provided that a rod with a widened head is employed.

(c) The length of the rod has very little influence on the measurement of elongation, provided that

<sup>1</sup> *Arbeiten der Kgl. Materialprüfungsamt*, 1900, vol. iv. p. 178. The first disc cut is centred in a ring of appropriate size, and the second disc cut from it. This second disc is centred as before, and the final disc and ring are then punched. By this double centring and treble cutting, both the outer and inner surfaces of the ring are punched under exactly similar conditions, which is not the case when only the disc from which the test ring is cut is centred.

<sup>2</sup> *Loc. cit.* Cf. Schidrowitz, *I.R.J.*, 1909, vol. xxxviii. p. 327.

the part of the rod actually tested lies well within the prismatic part.

2. *Ring-shaped Bodies.*—(a) The rings may be easily and accurately obtained.

- (b) The fixing of the rings in the machine and the carrying out of the tension experiment is much simpler and more reliable than in the case of rods.
- (c) Ring-shaped bodies tested on the Schopper machine require no observation during the experiment, and therefore save the time of the observer. In addition, the measurement of elongation is a great deal more difficult in the case of rod-shaped bodies.
- (d) For standard testing, the ring-shaped test body is preferable, because a perfect standard ring can be more readily agreed upon and be prepared than a rod. Moreover, the nature of the rubber frequently interferes in the case of the rod form.
- (e) Ring-shaped bodies give a better insight into the general tensile properties of the rubber than do the rod-shaped bodies during the course of the experiment.
- (f) In contradistinction to the rod, the ring can be employed for every kind of soft rubber.
- (g) No material differences with regard to the relative general characteristics of the different rubbers examined was found by comparing the ring and rod results except in the case of high class soft rubbers, where the breaking in the jaw, in the case of the rod bodies, obviously places the results out of court.
- (h) One apparent advantage which the rod-shaped body possesses, namely, that one may determine the tensile properties of a cloth or sheet longitudinally as well as vertically, is merely apparent, for by punching a number of rings

it is very easy to get the maximum and minimum values for any given sample.

- (i) Ring-shaped bodies give a better insight into the effect of a preliminary loading than do rods.

### *Method of Gripping Test Pieces*

In the experiments<sup>1</sup> of Memmler and Schob, referred to above, a "duck" jaw was used with the rod-shaped bodies. This is, however,<sup>1</sup> by no means the most suitable form of grip for the rod test piece. The best form, according to my experience, is a jaw constructed on the wedge principle. The question is not, I think, one of very great importance, for the experiments of the Prussian authorities so amply confirm the view which others, including myself, have expressed with regard to the superiority of the ring-shaped body working over rotating rolls, that where a free choice is possible, the verdict can scarcely be in question.

In connexion with the gripping or rather guiding of the ring-shaped body, Memmler and Schob<sup>2</sup> have made an exceedingly important observation, namely, that the ring must rotate around the guiding rolls during the experiment. In support of this view the following results—obtained with four different types of rubber—may be quoted :—

### RESULTS OBTAINED WITH ROTATED AND NON-ROTATED RINGS

Rubber Type.	Method.	Breaking Strain. (Kg. per cm. <sup>2</sup> ).	Ratio (rotated ring = 100).
<b>I</b>	Rotated	117.7	100
	Not rotated	60.4	51
<b>IIA</b>	Rotated	90.8	100
	Not rotated	21.5	24
<b>VA</b>	Rotated	97.1	100
	Not rotated	56.0	58
<b>VIIA</b>	Rotated	27.3	100
	Not rotated	24.7	91

*Note.*—Each figure represents the mean of fifteen experiments.

<sup>1</sup> Cf. Schidrowitz, *I.R.J.*, 1909, vol. xxxvii, p. 642.

<sup>2</sup> Hinrichsen and Memmler, *op. cit.*, p. 185.

*Machines and Apparatus for Tensile Tests*

The perfect testing-machine should, *inter alia*, answer to the following requirements:—

1. The test piece must be gripped so as to avoid (*a*) slipping and (*b*) crushing.
2. Total and intermediate loads, and corresponding elongations, must be readily and exactly determinable.
3. The elongation and load at the break must be automatically registered.
4. There should be no difficulty in applying an hysteresis test.
5. The machine must be sufficiently delicate to take small loads (say 100 grms. as a unit), and sufficiently powerful to deal with the most resistant material (say 100 kilos).
6. The machine must be capable of dealing with a wide variation in regard to size and shape of the test piece.
7. There should be no considerable initial inertia to be overcome, and the power must be capable of being applied gradually and steadily.
8. Preferably the machine should be of a vertical type, and errors of load eliminated by applying the force by means of a direct weight or lever.
9. The machine should be provided with an apparatus for reproducing the tension data in graphic form, *i.e.* for drawing curves automatically.

The above requirements apply to a machine for general tensile work. In the factory, where standard test sheets can be prepared, requirements 5 and 6 are of minor importance.

Figs. 25 *A* and *B* show very simple types of tensile strength apparatus. Fig. 25 *A* is that adopted by Stéwart in his classical experiments. In principle, as far as it goes, the machine is on correct lines. It is vertical; the application of weight is direct, and the test piece cannot slip, inasmuch as it is of the ring pattern. It, however, in no way detracts from the merit due to Stéwart for having evolved this simple yet effective piece of apparatus, to say that it is by no means

perfect. There is no guard, for instance, against the undesirable effects of lateral swaying, the application of the weights is a clumsy and unsatisfactory process, and elongation can only be measured with considerable difficulty at intermediate loads. There is no device at all for measuring the elongation at the break. The ring, moreover, is stationary, and, as Memmler and Schob have shown (p. 275), the results obtained with a non-rotating ring are liable to be very faulty. It must not, however, be inferred that the defects of Stévert's apparatus seriously effect the importance of his work, for the majority of the observations made by him were in connexion with intermediate loads.

Fig. 25 *B* represents in principle the type of apparatus employed by Pahl and Heinzerling in their well-known experiments. Except that it is vertical, and that the load is applied directly, this type has very little to recommend it. Thus, the pointers, by means of which elongation is measured, are more likely to

do harm than good, inasmuch as in this type of jaw slipping is sure to take place, and measurements of elongation therefore are bound to be incorrect. With strips, and with rings where there is no automatic device (such as that of the Schopper machine, for instance), the only correct method of measuring elongation is by taking, by means of callipers, the distance between two lines drawn on the test strip before starting the operation. It will be noticed that in the Pahl and Heinzerling apparatus there is also no guard against lateral swaying.

With a view, principally, to avoiding lateral movement

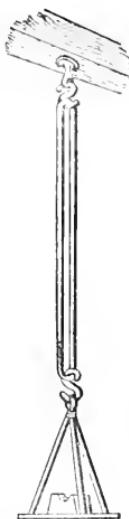


FIG. 25 A

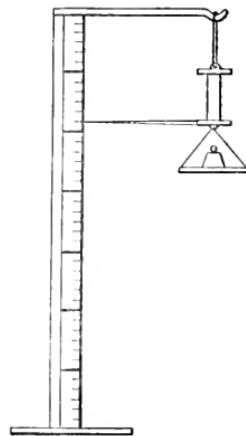


FIG. 25 B

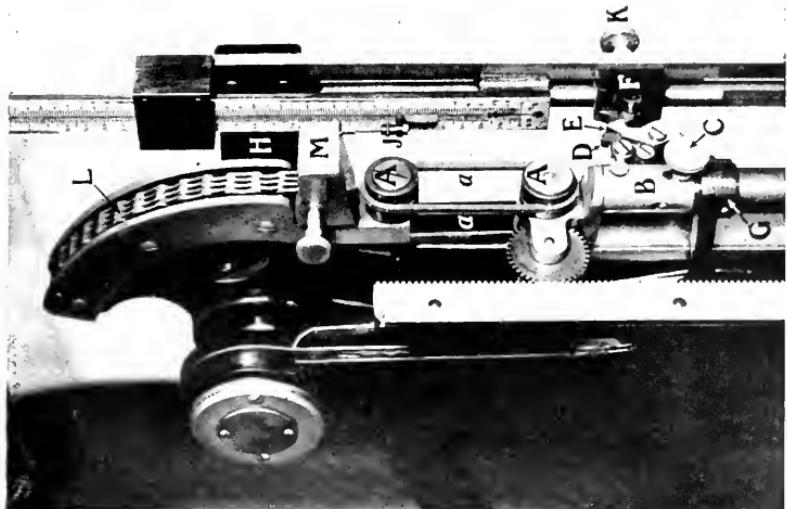
and improving the Pahl and Heinzerling type of apparatus, I devised, a number of years ago, the apparatus (intended for moderate and light loads only) shown on Plate XXXVIII. *B*. This apparatus may be used either with ordinary grips, or, where a ring-shaped test body is available, after the manner of Stévert, by suspending the ring over and between the hooks shown in the figure (attached to the cross-bar *D* and cage *C* respectively). The collapsible canvas bag *A*, running by means of eyelets with a minimum of friction over the polished uprights *B B*, is weighted with shot, the latter being run in from the container *E*. In the case of a ring-shaped test body, elongations may be read directly by means of the scale and pointer; with test strips, the callipers method must be adopted. When the test piece breaks, the bag *A*, on striking the canvas-covered box bottom, collapses easily, and no shot is spilled. The total load at break may be ascertained by running the shot out of the bag *A* and weighing, or alternatively, definite weighed increments of shot may be added. The separate piece of apparatus, *F G H*, is used for determining the "coefficient of resiliency" or limit of elasticity, as described elsewhere.<sup>1</sup> The apparatus obviously possesses all the defects—so far as determination of actual breaking strain and elongation at break are concerned—associated with the use of a jaw grip or a stationary ring. I still employ this apparatus occasionally for "breaks," but only when the specimen to be tested is too small for testing on the Schopper machine. It is also useful for the estimation of elongations at constant load, for which purpose the Schopper machine is not adapted.<sup>2</sup>

#### *The Schopper Machine*

Plate XXXIX. is a general view of the Dalén-Schopper machine; Plate XXXVIII. *C* shows details of the more

<sup>1</sup> P. 234, and *J.S.C.I.*, January 15, 1909.

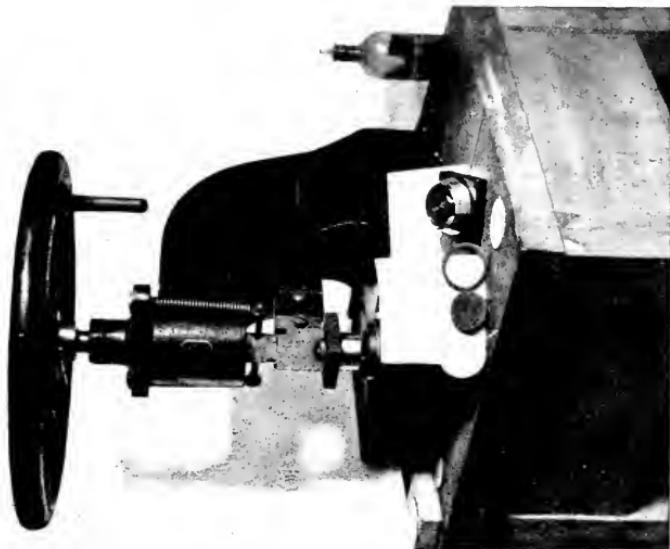
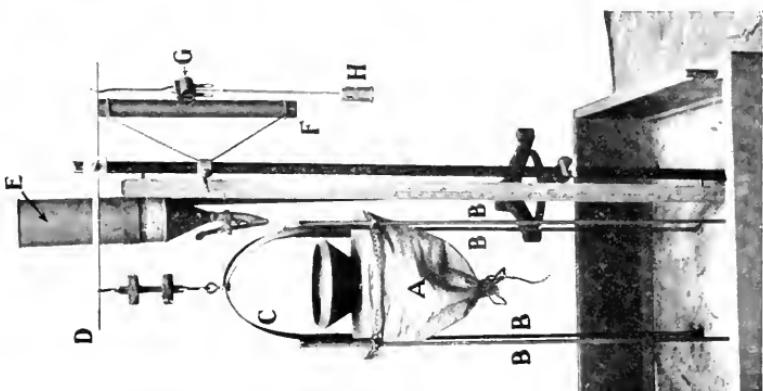
<sup>2</sup> An apparatus for determining elongation at constant load, designed by Prof. Martens, and constructed by Schopper, is described in Hinrichsen and Memmler, *Der Kautschouk*, etc., p. 214. It may also be used for measuring "set" after a constant load or constant elongation, etc.



C DETAILS OF SCHOPPER TESTING MACHINE  
(SEE P. 277)

B SIMPLE RUBBER TESTING APPARATUS  
(SEE P. 278)

A SCHOPPER APPARATUS FOR CUTTING TEST-RINGS  
(SEE P. 271)





important working parts. The apparatus (cf. Plate XXXIX.) is worked by hydraulic power (a pressure of about 40 lb., *i.e.* that of an ordinary main, sufficing), the water entering at O and passing away at P. By means of the reversing valve K, water can be admitted either at the bottom or top—*i.e.* below or above the piston head—of the cylinder A. In this way the rod A rises or falls as desired, stretching or relaxing the rubber band under test, as the case may be. The actual pull is communicated to the lever G, by way of the top roll A, by the chain H (A and L in Plate XXXVIII. C), and the friction of the piston rod does not, therefore, come into consideration. The load is measured on the scale J (100 kilos subdivided to 0.2 kilo), by means of a knife edge attached to the lever. The latter comes to rest at any point at which the pull ceases, and is then kept in position by a series of narrow teeth M. While the rubber test ring is being adjusted on the roller, the lever is fixed by means of a jaw, which is subsequently released by turning the handle N. This is necessary in order that the adjusting operation as such shall not cause a preliminary pull. The actual operation of making a tensile experiment is (Plate XXXVIII. C) as follows: The piston rod is allowed to ascend to its maximum, and the collar B, to which is attached the lower roll and gear A and release D, E, is raised and secured by means of screw C. By bringing the scale H into position with screw K and the sliding rod, and forcing down the spring hammer D, the release E is brought to a vertical position and engages the support F of the sliding scale. The final adjustment of the scale with the vernier J may now be made, and the ring test piece *aa* is stretched over the rolls A A. The top roll is loose and revolves on ball bearings: the lower roll is caused to rotate by the gear shown. The result is that as the ring is stretched it also rotates, and in this way every part of the ring is successively exposed to an equal strain, and any crushing effect is avoided. The piston is now caused to descend slowly, the rate being adjusted by tap L (Plate XXXIX.). As the lower roll (Plate XXXVIII. C) a de-

scends, the scale H is correspondingly moved, and the load is measured by the swaying out of the lever. When the ring has been stretched so as to become quite taut, the screw C is loosened, with the result that collar B, with the attached release gear and lower roll, are now supported by the rubber test ring itself. When the ring breaks, the collar B drops, the release E flies back, and is so disengaged from F. The piston continues its descent (subject to being stopped by cutting off the water supply), but the scale H, of course, stops at the breaking point, as does also the load-indicating lever.

The scale H is a double one, and permits readings of the actual extension, and of the latter expressed in percentages of the original length of the ring.

The dimensions of the standard ring employed on the Schopper machine are: Outer diameter, 52.6 mm.; breadth, 4 mm.; height, 5 mm. The punching apparatus, however permits of the cutting of rings from material varying in thickness from 1 to 5 mm. The scale permits of an elongation of 10 diameters, which is sufficient for the majority of rubbers. Very soft materials, however, will stretch beyond this limit, and the latest machines, are, I believe, being made with a longer scale. The apparatus may, if desired, be used for testing rod-shaped bodies, and with this end in view provision is made for replacing M (Plate XXXVIII. C) and the lower roll and gear with suitable fittings.

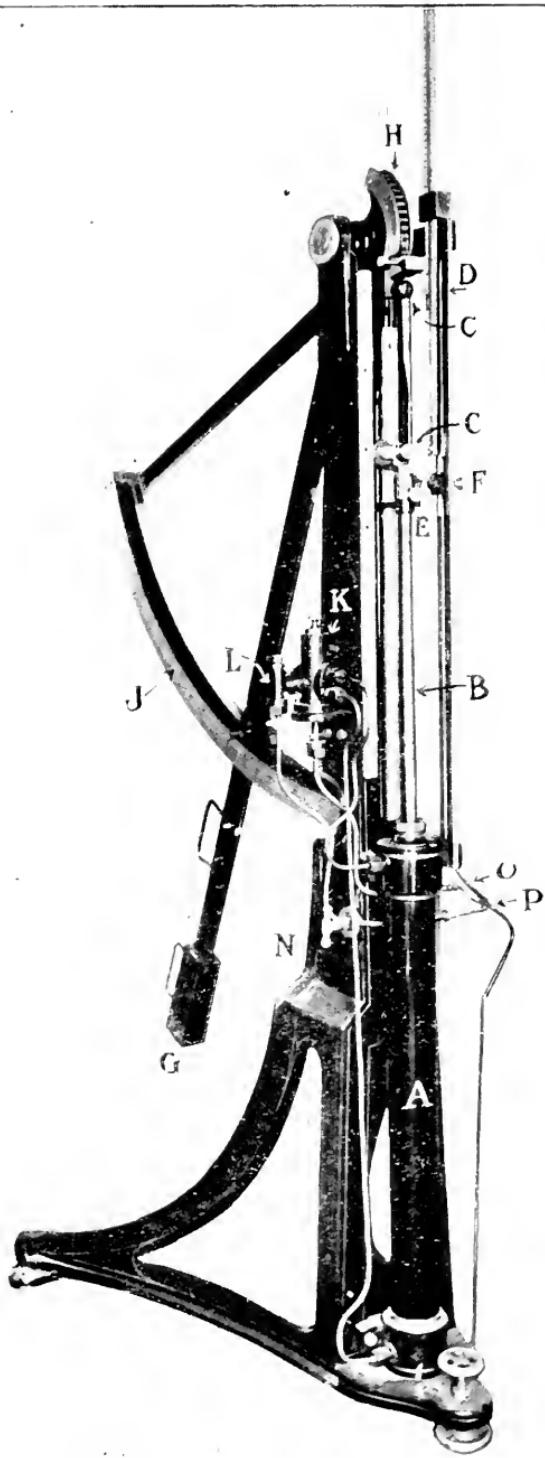
A disadvantage of the machine, as originally designed, is the absence of any provision for reproducing the tension data in graphic form, but the machines of the latest design are fitted with a curve apparatus.

*Horizontal Machines* have been designed by Delaloe,<sup>1</sup> A. D. Cillard Fils,<sup>2</sup> Beadle & Stevens,<sup>3</sup> and others.

<sup>1</sup> Cf. Schidrowitz, *I.R.J.*, 1909, vol. xxxvii. p. 564.

<sup>2</sup> Hinrichsen and Memmler, *op. cit.*, p. 198, and *Le Caoutchouc et la Gutta-Percha*, 1907, p. 1061, *et seq.*

<sup>3</sup> *J.S.C.I.*, 1909, p. 1111.



SCHOPPER MACHINE FOR 'TENSILE' TESTS  
(SEE P. 278)



*Schwartz' Hysteresis Machine*

Prof. Schwartz<sup>1</sup> has designed a machine for obtaining hysteresis curves, particularly with a view to testing "flexible" strip. A diagram of the machine is shown in Fig. 26.

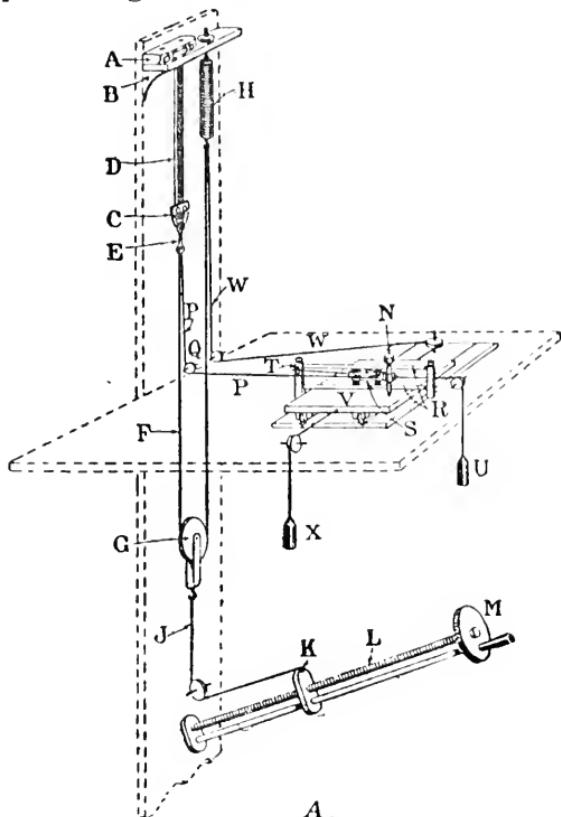


FIG. 26.—Schwartz' Hysteresis Machine

The following description of the machine and method of use are quoted from Schwartz' paper:—

"The test piece having been secured in the grips, the fixed grip A is mounted on the pins on the bracket B, and the movable grip C, which depends from the specimen D, is connected by the removable hook E to the cord F, which passes round the floating pulley G to the helical spring H;

<sup>1</sup> *Journ. Inst. Elect. Engin.*, 1910, p. 701.

the load is applied and withdrawn by the up and down traverse of the pulley G, which is effected either by means of a small hydraulic cylinder, the rate of movement of the piston of which is controlled by a bypass; or, as shown in the figure, by the cord J, which is attached to the nut K, which is moved along a guide by the screw L, which is turned by hand at M.

"It will be seen that an even rate of motion of the pulley G does not necessarily result in an even rate of extension or retraction of the test piece, nor in an even rate of increase or decrease in the load upon it. Since the movement of the pulley G is shared between the test piece and the spring H, the action is a differential one, the extension of the spring being directly proportional to the load, while that of the test piece depends upon the nature of the rubber under test. Provided, however, that the rate of movement of the pulley G is kept within certain limits, the results obtained are identical with those produced by increasing the load at a constant rate.

"The relation between load and extension is charted in the following way: The grip C, the movement of which represents the extension, is connected to the pencil carrier N by the thread P, which passes over the pulley Q. The pencil carrier, which moves between the guides R, contains a pulley S, round which the thread P passes to a stop T, which is adjustable as to position, where it is made fast. The movement of the pencil is thereby reduced to one-half of the extension of the specimen. If necessary this movement may be again reduced by one-half by the introduction of a light floating pulley in the thread P. The movements of the pencil carrier are controlled by the counterweight U. Beneath the pencil carrier, and moving at right angles to it, is a light table V, on which a chart paper is fixed; the movement of this table is directly proportional to the load, as it is attached to the spring H by means of the thread W. The movement of the table is controlled by the counterweight X."

The machine, which I have seen in operation, is well

suited for the particular purpose for which it was designed, namely, that of rapidly gaining an insight into the character of samples of commercial "flexibles." With regard to its use for general rubber work, it possesses the disadvantages of all machines working with jaw grips or stationary rings, and, as it is very lightly built, the hysteresis curves obtainable lie within somewhat narrow limits.

Martens<sup>1</sup> has designed an apparatus for simultaneously testing four rings by repeated elongation. The machine is motor-driven, and is provided with a "counter" for registering the number of stretchings. The A. D. Cillard Fils<sup>2</sup> apparatus, which was designed with a view to testing other materials (yarns, cords, linoleum, celluloid) besides rubber, permits of the making of repeated elongation and repeated bending, abrasion, compression, etc., tests, but in regard to purely tensile tests, the remarks which I have made concerning the disadvantages of "jaw" or stationary ring machines apply.

The tensile tests which may be applied to rubber goods may be summed up as follows:—

Breaking strain; elongation at break; nature of curves at intermediate loads and up to break; minimum load producing specific sub-permanent set; elongation with constant load; load supported at constant elongation; effect of varying load and time on sub-permanent set; effect of repeated elongations, etc.

Hysteresis test—Form of loop; area of loop; ratio sub-permanent set: work done, etc.

Determination of various coefficients (cf. pp. 220–238).

### B. COMPRESSION TESTS

The general lines on which compression tests should be carried out have been indicated by Stévart.<sup>3</sup> The compres-

<sup>1</sup> Memmler and Schob, *loc. cit.*; and Hinrichsen and Memmler, *op. cit.*, p. 212.

<sup>2</sup> Cf. reference, p. 280.

<sup>3</sup> *Loc. cit.*, p. 221.

sion tests ("plates" test, repeated compression test, hammer test) which are frequently specified in railway contracts for buffers, buffer rings, etc., are purely empirical, and merely show that, for instance, a certain buffer or set of buffers are free from flaws and of a certain general character.

If a certain specific buffer happens to have a mechanical flaw, this will be detected by the tests at present used, and this may lead to a total rejection of the goods. In an article such as a buffer, a flaw is, as likely as not, due to a fault in one particular mould. The mixing, as a whole, may be perfectly satisfactory. It is fairly obvious, then, that tests which give no information concerning the general nature of the material from which the article is made, but merely some relative information regarding the behaviour of a particular sample, leave much to be desired.

I do not suggest that the empirical—but, *faute de mieux*, certainly useful—tests referred to should be abandoned, but it appears to me eminently desirable that they should be supplemented by tests from which the general character of the material can be deduced. In this connexion the determination of Stéwart's compression constants (by plotting load against height, etc.), and of the general tensile properties of the material would, I believe, lead to exceedingly valuable results. To discuss this aspect of compression testing further has at present little value, owing to the meagreness of the available data. The nature of the empirical compression tests employed in practice may be gathered from the following quotations from existing specifications:—

*Quotations from Specifications for Compression Tests*

1. *The rubber shall stand the following tests:—*
  - (a) *Compression to half thickness for a period of forty-eight hours without permanent set or fracture. . . .*
  - (b) *10,000 compressions to half thickness (i.e. about fourteen compressions per minute).*

- (c) 500 blows of 50 cwt. within twelve minutes, without set or fracture.
- (d) The static resistance of the rubbers to be the same after the tests as before, and the rubbers to remain perfect.

2. *Buffers.—Test loads.*

- 7 inches diameter  $\times$  2 inches thick  $\times$  2 inches; test load,  $3\frac{1}{2}$  to 5 tons.
- 5 inches  $\times$  2 inches;  $\times 1\frac{7}{8}$  inches; test load, 5 to 7 tons.
- $4\frac{1}{2}$  inches  $\times 1\frac{1}{2}$  inches  $\times 1\frac{1}{2}$  inches; test load, 4 to 6 tons.

3. *Specification for Buffer Springs.*

- (a) In the form of a spring, the resistance, when compressed to half thickness, shall be one ton for 3 inches of area.
- (b) The spring shall be compressed to half thickness for 120 hours, after which it shall return within one hour to its original dimensions without fracture or set.
- (c) The spring is submitted to 10,000 blows, at the rate of 60 per minute, the temperature being taken between each 2500 blows, and if found to exceed  $212^{\circ}$  F., the spring to be allowed fifteen minutes for cooling. The spring to withstand this test without fracture or set.

### C. ABRASION TESTS

A number of devices have been suggested for examining the resistance of rubber to abrasion. As a rule, these consist in pressing the specimen against a rotating emery or carborundum wheel. In some cases the pressure is applied by means of a dead weight, in others by a lever. It is by no means an easy matter to obtain reliable abrasion results, the steady holding of the specimen and its adjustment causing considerable difficulties. I have recently had con-

structed a little piece of apparatus, which, so far, has given very fair results. This is shown in diagrammatic form in Fig. 27. The test piece employed is in disc form, and is obtained by punching from a sheet with the Schopper cutter.

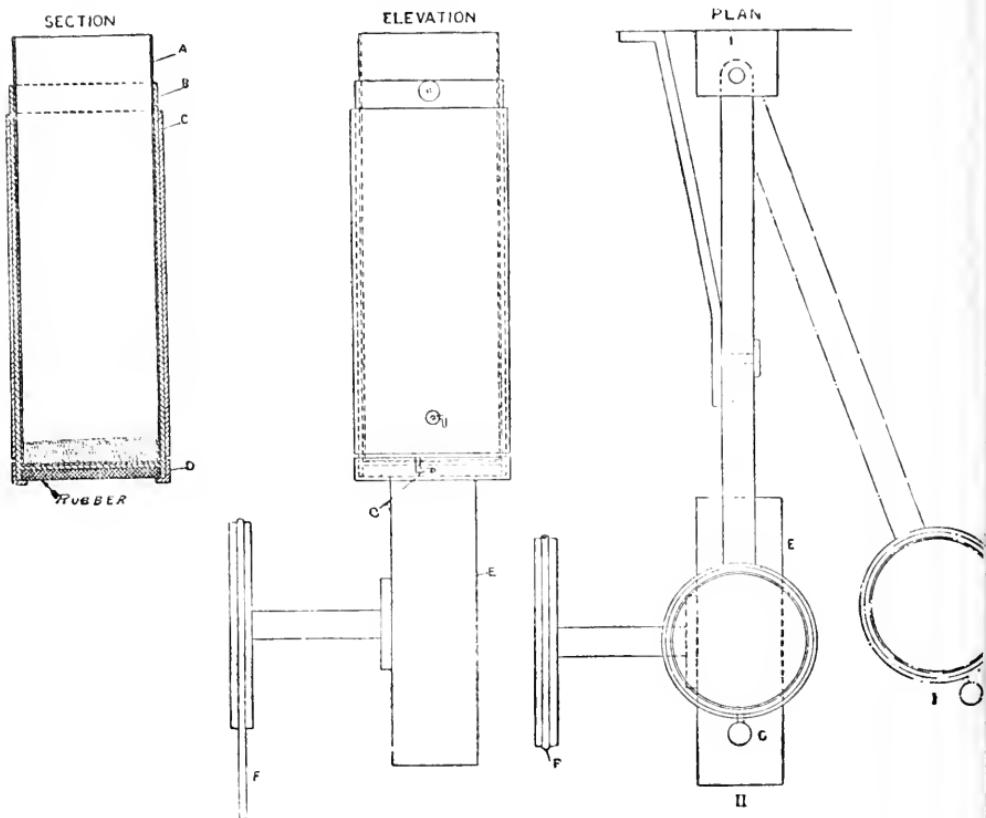


FIG. 27.—Abrasion Apparatus

A, tube weighted with shot; B, holder for rubber; C, outer casting; D, detachable cap with bayonet-joint for maintaining rubber in position; E, abrading wheel, power driven by means of pulley F. After swinging into position (Plan II) over wheel, B is let down by giving a half-turn to catch G

Should the material be thinner than 5 mm., the disc is built up to the latter thickness by means of thin cardboard discs, and in this manner a very fair adjustment may be obtained. The inner tube A is weighted with shot to an appropriate load. After the rubber disc has been fixed in position by

means of the collar D, the tube is swung over the abrading wheel E, and may be released and let down on to the wheel at any desired moment by giving a half-turn to the catch G. The wheel is driven from a shaft by means of pulleys and a cord, F, at an approximate speed of 30 revolutions. For most purposes a standard time of 30 to 45 seconds gives satisfactory results. The discs are weighed before and after the experiment, the difference being a measure of the abrasive effect.

An ingenious abrading machine for use with ball specimens has been devised by Martens.<sup>1</sup> The abrasion effect is obtained by means of a weighted pulley rotating horizontally round a fixed axis over a solid base in which, and close to the periphery, a circular gutter has been drilled. The balls are placed in the gutter, and are carried round by the abrading disc. The abrasive effect is measured by the loss of weight after a given time.

#### D. OTHER TESTS

*Hardness* is conveniently measured, according to Cillard, by determining the force necessary to drive a pointed metal cone a certain distance into the test material; *elasticity* by measuring the height of the rebound of a steel ball from the material into which it has been dropped from a fixed height.

<sup>1</sup> Hinrichsen and Memmler, *Der Kautschuk*, etc., p. 211.



## APPENDIX

### CONTRACTS AND SPECIFICATIONS<sup>1</sup>

#### MAIN CAUSES OF DIFFICULTIES BETWEEN MANUFACTURERS AND CONSUMERS

THE enormously varying nature of the requirements of the consumer and his frequent lack of knowledge of the essentials of the science and technology of rubber manufacture, on the one hand, and the stress of competition, and to a minor degree inexact information as to the actual requirements of the consumer, on the other hand, may be fairly regarded as the roots of the difficulties which lie in the path leading from the manufacturer to the consumer. There are many consumers who have only the vaguest ideas as to the various qualities of raw rubber; in fact they appear to think that there is only one quality of rubber—namely, fine Para—which is of any value, and that all the rest is rubbish. As a result they frequently insert the words “fine Para” in a specification and thereby make it impossible for the manufacturer to supply a fair article at the price required. As likely as not, too, there is not the slightest necessity for the employment of fine Para in the article in question. To the consumer, then, unfortunately, all rubber is either equal or it means only fine Para, and he fails to appreciate the fact that for different articles entirely different mixings and methods of manufacture generally are required. Again, one frequently finds that the consumer is extremely reticent in regard to the information which he gives the manufacturer with regard to the actual purpose for which he requires the goods; or, again, he may give a general,

<sup>1</sup> The matter under this heading is extracted from a paper read by the author at the 1908 Rubber Exhibition Conferences. The complete paper was published in the official report of the Exhibition Conferences and in the *I.R.J.*, 1908, vol. xxxvi. pp. 345 *et seq.*

but not a specific, indication; or he will insert particulars which are irrelevant, and leave out others which are most important; or, again, he will insist on applying a particular test or a series of tests, useful enough for a certain class of goods, but useless, or even misleading, in regard to others. On the other hand, stress of competition or lack of exact knowledge on the part of the consumer may induce some manufacturers to produce articles which are inferior or unsatisfactory. The consumer naturally desires to obtain the best article at the lowest price, but his frequent lack of knowledge of what a fair price is for the best article leads him to accept a tender at a price at which a good article cannot be produced. To my knowledge it is an everyday occurrence that manufacturers of high repute refuse to undertake the manufacture of certain articles at a given price, but there are others who are not so particular.

#### LOW PRICES WHICH LEAD TO DISCARDING OF RUBBER GOODS

Strenuous competition, or, as it is regarded by the high class manufacturer, unfair competition, on the lines indicated above, results occasionally in a consumer discarding rubber altogether and replacing it by other substances, such as glass or metal. The fault as often as not lies originally with the consumer, who has insisted on obtaining rubber goods at a price which for his particular purpose is impossible. He obtains the goods, finds that they are unsatisfactory, and then proceeds to condemn rubber goods generally. I have in mind a particular instance within my own knowledge where this has occurred on a very large scale. In this particular instance rubber has been entirely replaced by metal. I think that if the consumer had been willing to pay a slightly higher price he would have obtained a rubber article which, besides being more suitable for his purpose than metal, would in the long run have turned out to be cheaper. In certain classes of work it is well known that firms of the highest class have come to an understanding not to manufacture certain goods under certain prices, and in this particular line the consumer is now well aware of the minimum price at which he may expect a good article. There is no reason apparent why manufacturers of other classes of goods should not take similar steps to inform consumers of the true state of affairs.

## TENDERS—ON SAMPLE OR SPECIFICATION

I think, then, that it will be admitted that the chief factor in determining easier relations between the manufacturer and the consumer is that the consumer should be quite clear as to what he really requires, and that he should make his requirements equally clear to the manufacturer. This brings me to the thorny question of samples and specifications. Should goods be ordered according to a certain sample, or should they be required to come up to the terms of a specification? I think that manufacturers are practically unanimous that the old method of ordering on sample, without a specification stating in what regard bulk is to correspond with the sample, and by what tests similarity of bulk to the sample is to be controlled, is to be condemned. Nevertheless, certain consumers still order goods in this way. The sample is frequently so old or deteriorated that it is of no practical value to the manufacturer, and in such cases the latter must always be more or less in the dark as to whether the goods that he is manufacturing will be satisfactory or not. I have in my mind in this connexion certain of the great railway companies—who ought to know better—who order sheet goods in this manner, and also certain classes of cable coverings.

## CONTRACTS ON SAMPLE ALONE

The disadvantages of this method are fairly obvious. To begin with, all samples are liable to deterioration both as regards quality and pattern. Assuming, however, that the sample has not deteriorated, it is frequently a matter of great difficulty for a manufacturer to match a sample in such a manner as to fulfil the requirements for which the goods are intended unless he has received clear information on this point. The general opinion among manufacturers and enlightened consumers appears to be that sale on sample alone is bad, but that sale on sample, provided that it is stated clearly in what respects bulk must correspond to sample, is a good method. A moment's consideration will show that in a sale on sample governed by a specification the sample constitutes, in most cases, no more than an excellent guide, and the crux of the question lies really in the particulars of the specification. In regard to the latter, again, the methods by which bulk and sample

are to be compared to ascertain whether the specification has been complied with, may be of vital importance. It is freely admitted even by manufacturers, who suggest that lower grade goods might be sold to sample alone, that difficulties do arise in this regard owing to differences of opinion between the manufacturer and the consumer, particularly in regard to the extent of deterioration, which should have been allowed for in the sample. Again, the experience of some consumers is that in the case of goods ordered to sample alone, the bulk may superficially resemble the sample, but on closer examination turn out to be of very inferior quality.

#### CONTRACTS ON SPECIFICATION ALONE

As a general rule, contracts made on specification alone are unobjectionable, provided the specification is clearly drawn, that it embodies all the consumer's requirements, and that it contains no elements of an irrelevant or disturbing nature to the manufacturer. For instance, I should describe as irrelevant and disturbing elements such terms in a specification as "properly vulcanized rubber," "best quality," "pure Para," or "virgin rubber," without further qualification or elucidation of such terms. It is undeniable that the method of tender by combined sample and specification is desirable in most instances, but unless the sample is in such a condition as to give a fair indication of its original quality it is liable to do more harm than good.

#### THE TERMS "PURE PARA," "BEST RUBBER," "PROPERLY VULCANIZED," ETC.

I have referred in the above briefly to the objectionable nature, from the manufacturer's point of view, of such terms in specifications as those in the heading of the paragraph. At the risk of being accused of iteration I would say a few more words on this subject. Many consumers do not appear yet to understand that there are many other qualities of rubber besides fine Para, and that for many purposes some of these rubbers may be equally satisfactory to, and in others more satisfactory than, pure Para. For instance, where great strength and resilience are required pure Para cannot be bettered, but even in this regard there are certain rubbers, other than Para, which are for many practical purposes

sufficiently strong and resilient, yet which are of decidedly lower price. In other instances fine Para may actually be less desirable than a lower class rubber; thus in certain cases it is desirable to have a rubber which contains rather more resin than the fine Para. A consumer, therefore, who without reference to his actual requirements strives to pin down the manufacturer to fine Para, will as likely as not receive an inferior article for his purpose compared with that which he might have had if he had given the manufacturer a free hand in this regard. It may be inferior for a variety of reasons. In the first place Para may be unsuitable for the article, or the high price of Para may conduce to an inclusion of an excessive amount of mineral matter, not to speak of remade rubber or rubber substitutes, in the article. Again, the term "best rubber" may mean anything or nothing. A consumer may thereby mean Para or merely rubber unmixed with any other hydrocarbon. The term "properly vulcanized," which is made in many specifications, is likewise, in my opinion, an objectionable one, as it is capable of giving rise to interminable controversies, and is in itself a suggestion that the manufacturer is likely to shirk the most important part of his business.

#### TESTS SPECIFIED AND OTHERWISE—GENERAL CONSIDERATIONS

It is obvious that a specification which is to be of any value must be governed by tests which show whether the specification has been complied with. In specifying tests, and they should most certainly be specified, it is most desirable that the consumer should bear in view two main considerations, and these are: (1) They should be suited to show that the methods employed for making the article are such as to give the best results for endurance, etc., under the normal conditions to which they would be subjected; (2) they must be of a practical nature and of such a character as to show whether or not the specification has been complied with.

Stated as abstract propositions the two above conditions for tests to govern specifications appear to be obvious truisms. It is, nevertheless, remarkable that in practice the principle underlying them is frequently disregarded. It is obvious that tests which are suitable, for instance, for railway buffers or springs, may be totally unsuited for the purpose of ex-

amining goods which are to be subjected to high temperatures, or that goods which are intended for electrical purposes should be subjected to tests which were devised for the testing of goods where great strength and resiliency are the main considerations. Such tests may not only be useless, but they may be absolutely misleading. Perhaps the most glaring instance is the application of the heat test to all kinds of mechanical goods which are never intended to be subjected to any extreme of temperature. Before the saponification test was devised the heat test was useful for all classes of goods, as it clearly indicates the presence of some oily or fatty substitutes. The real object and origin of the test is now frequently overlooked, hence the application of this test in many specifications which are not to be subjected to heat, with the absurd proviso to the effect that the properties of the goods are not to be altered in any way by the test.

#### OPINIONS OF MANUFACTURERS AND CONSUMERS ON MECHANICAL TESTS

The opinions of manufacturers and consumers, particularly in the railway, electrical, and elastic strip industries, are on the whole decidedly in favour of mechanical tests. They appear generally to recognize the fact that such tests should be very carefully specified and agreed on between the buyer and seller, and that they should be adapted to the particular class of goods. In the abstract this amounts to an agreement that these tests should be mainly specific, but in view of the many unsatisfactory specifications which one comes across it would appear that some sort of general idea regarding the details and methods of testing goods which are not specified, for instance, such as those briefly indicated above, should be considered by the general body of manufacturers and consumers.

#### ELECTRICAL TESTS

The electrical tests for telegraphic, telephone, and lighting work respectively are now practically of a standard nature, and in any case the consumer as a rule is in a position to know exactly what he requires in this connexion. No great difficulty arises, therefore, in connexion with such tests. The point worth consideration, therefore, is whether electrical tests suffice. Many consumers now recognize the fact that

electrical tests alone, without mechanical, or heat, or chemical tests, are insufficient, as the goods when new may show perfect electrical results and yet deteriorate rapidly for reasons which would have probably been disclosed by the other classes of tests. To go into the details of what such tests should be would carry me too far, as they would involve the consideration of an enormous amount of detail. The general principle of suiting the tests to the goods in question applies here as in regard to other industries.

#### HEAT TESTS

These tests have perhaps more than any other given rise to discussion, and particularly is this the case in regard to the moist heat test. Although this test was abandoned by the Admiralty in 1905 and replaced by a chemical test it is still found in many specifications, and there is no doubt that it is high time that as a promiscuous test for all classes of goods it should be abandoned. There certainly appears to be a general consensus of opinion among manufacturers that the heat tests used promiscuously are objectionable, but, as might be expected, that they are useful in specific instances where the conditions of use are such as to involve high temperatures. I have already alluded above to the fact that the object for which the moist heat test was devised can now be attained in a much better manner by a chemical test, namely, the saponification test. It is remarkable that one still comes across specifications in which it is stated that goods (of the most varying nature) are to be tested by the dry and moist heat tests, and that these are to be examined for tensile strength, etc., before and after these tests have been applied, and that such tests are not to cause any deterioration. I doubt whether a sample of india-rubber goods has ever been produced which would literally comply with this demand. It is obvious, from a purely theoretical consideration of the nature of vulcanization, that this cannot be the case. It follows then that the amount of deterioration permissible must be left to the judgment of the consumer or his inspector, and this is scarcely a satisfactory state of affairs.

#### OTHER PHYSICAL TESTS

Other physical tests which require some discussion are those for estimating specific gravity, porosity or permeability,

and the sun-cracking test. In regard to specific gravity there is no particular difficulty, but I think that the old-fashioned method of working a liquid up to the density of the material should be discarded, and that the more exact method of the specific gravity bottle should be more universally adopted. With regard to porosity, I have found some difficulty in applying the method devised by Weber, and have obtained better results in this connexion by means of a method, the principle of which is that the air is driven from the pores and replaced by water by a process of boiling. This method is not perhaps unobjectionable, but in most cases gives better results than the ordinary porosity methods. With regard to the sun-cracking test, this is really a chemical rather than a physical test, and I am inclined to think that as it is described by Weber it is somewhat disappointing. It is possible that the method devised by Ditmar of treating the sample under pressure with oxygen may give better results. For the present I think that this test is not one which can be standardized or generally adopted.

#### CHEMICAL TESTS

The chemical tests of utility concerning which differences of opinion may arise are those for ascertaining the saponification value, the mineral matter, and the various forms under which sulphur exists in the goods. With regard first of all to the saponification test, it is generally considered by manufacturers and others that this test should be standardized rather more fully than is the case, for instance, in the Admiralty specification. In my opinion the test would be of much greater value both to the manufacturer and to the consumer if the saponification test were preceded by an estimation of the resinous matter and free sulphur by acetone extraction, etc., and its application to the extracted rubber. The maximum amount of resinous extract and of free sulphur could then be specified if necessary. With regard to the estimation of mineral matter, some standard method either of incinerating the material or of destroying or separating the organic matter by other means is clearly desirable; for, although in most cases simple incineration gives a very fair result, I have known cases where differences of as much as 14 to 15 per cent. between the actual mineral matter and that obtained by ordinary incineration have occurred. I admit that such

differences should not occur in the laboratory of anyone familiar with rubber goods, but the determination of mineral matter is apparently such a simple operation that it is frequently entrusted to those who have no particular experience in this direction. With regard to the estimation of sulphur in its various forms, manufacturers generally appear to be of opinion that standard methods are desirable. With regard particularly to the relation of the manufacturer to the consumer in this connexion, I may perhaps be permitted to point out that the proviso contained in many specifications (including the Admiralty specification) that the goods are not to contain more than  $x$  per cent. of total sulphur, is only of relative value. The important factors are clearly (*a*) the amount of free sulphur and (*b*) the amount of sulphur combined with the actual rubber. The sulphur limit in specifications as it stands may on the one hand be unjust to the manufacturer, particularly in the case of high class goods, and on the other hand may be misleading, as far as the consumer is concerned. It is very necessary to point out that the endurance of rubber goods is appreciably affected by the amount of free sulphur present, although, of course, this factor varies according to the actual class of the goods. The general character of the goods is also dependent on the amount of combined sulphur, and the determination of this—not always an easy task, it must be admitted—frequently gives valuable hints as to the nature of the faults with which the goods may be endowed or their probable behaviour under certain conditions. There are many other chemical tests for determining either qualitatively or quantitatively the various ingredients of rubber mixings, but these tests are as a rule not employed in the case of contracts, but merely for special purposes with a view to ascertaining as nearly as possible the exact composition of a rubber article or the cause of failure, etc. It is not necessary to enter into them in any detail. The general methods of analysis may be ascertained by reference to the literature bearing on the subject.

#### SAMPLING AND INSPECTION OF GOODS

Difficulties are likely to arise in this connexion if it is not mentioned specifically in the contract what number of items should be taken for testing, how they should be taken, where the inspection is to take place, and so on.

**LIMITATION OF INGREDIENTS IN THE MIXING—(a) WITH REGARD TO THE QUALITY OF THE RUBBER**

Although many consumers still adhere to the "pure Para" shibboleth, manufacturers appear to be unanimous in their opinion that the quality of the crude rubber employed should be left to their discretion. I think it may be fairly asserted that in this regard the manufacturer is absolutely right, and that he may be trusted to use the most appropriate quality of rubber for producing at the lowest price the article required. It is true that here and there the manufacturer may strive to cut prices by using inferior grades of rubber for high class articles, but such a proceeding is bound to have disastrous results to his trade in the long run.

**(b) AMOUNT OF MINERAL MATTER**

The amount of mineral matter in a mixing is frequently specified, and in some instances rightly so. In other instances the nature of the mineral matter is specified. On the whole there is no great objection, where there is a really good reason for the proviso, why the quantity of the mineral matter, and occasionally its quality—provided that the specification is clearly worded in this connexion—should not be demanded, but unless the consumer has special experience in this connexion he will do well to leave the initiative in this regard to the manufacturer.

**(c) RUBBER SUBSTITUTES AND RECLAIMED RUBBER**

There can be no doubt that for high class goods substitutes should be prohibited, but in regard to reclaimed or remade rubber, particularly where lower grades of goods are in consideration, the consumer will do well to think twice before objecting to their employment, as he may thereby in the long run obtain an article inferior to that which he would have obtained if he had made no such proviso.

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